High performance magneto-optic garnet materials for integrated optics and photonics

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High Performance Magneto-Optic Garnet
Materials for Integrated Optics and Photonics

By
Mohammad Nur E Alam

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

at
Electron Science Research Institute
Faculty of Computing, Health and Science

EDITH COWAN UNIVERSITY

Supervisors:
Prof. Kamal Alameh & Dr. Mikhail Vasiliev

September 2012
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I lovingly express thanks to my beloved wife for being a constant source of support with patience, understanding and encouragement for the past two years and also like to convey the heartiest love to my daughter Nazah Nur.
PUBLICATIONS

Journal Articles:


Refereed International Conference Publications:


Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ with low coercivity for applications in integrated optics, imaging and sensing devices,” in Proc. Int. Conf. on High-capacity Optical Networks and Enabling Technologies Conference 2010, pp- 62-66, December 19-21, 2010, Cairo, Egypt.


Certificate for the Publications

This is to certify that Mohammad Nur-E-Alam is one of the active co-authors for the following published journal articles. The articles details are as follows:


He worked for these publications by taking part in the preparation and characterization of thin film garnets and garnet-oxide composite samples and also by finalising many of the obtained characteristics and results. Personally I have a high regard for his contribution to the publications and also grant him permission to refer to these articles as part of his research.

Dr. Mikhail Vasiliev

Signature:

Date: 28th of August, 2012.
ABSTRACT

This work explores the preparation, characteristics and properties of highly bismuth (Bi) substituted, metal doped, iron garnet compounds and investigates their potential for various emerging applications in the visible and near infrared spectral regions.

Bi-substituted iron garnet and garnet-oxide nanocomposite films of generic composition type \((\text{Bi, Dy/Lu})_3(\text{Fe, Ga/Al})_5\text{O}_{12}\) are prepared by using a radio frequency (RF) magnetron sputtering technique. The physical properties (crystallinity, film morphology, optical absorption spectra across the visible spectral range and the elemental composition of layers), and magneto-optic behaviour (Faraday rotation, hysteresis loops of Faraday rotation, and magnetic switching behaviour) of these sputtered garnet films are investigated in this work. These garnet materials possess high-quality nanocrystalline thin-film microstructures and demonstrate excellent combination of optical and magneto-optical (MO) properties which makes them very attractive for use in magneto-optical applications. Record-high MO performance, in terms of the material’s MO figures of merit achieved (which exceeded most or all of the values reported previously for any semi-transparent MO materials across most of the visible spectrum), is achieved simultaneously with high Faraday rotation, making them suitable for a wide range of applications in integrated optics and photonics. The effects of annealing on the garnets of type \((\text{Bi},\text{Dy})_3(\text{Fe},\text{Ga})_5\text{O}_{12}\), when performed in air atmosphere, are investigated and a systematic study is conducted to figure out the annealing behaviour and the crystallization kinetics of garnet formation within the garnet-bismuth oxide nanocomposites. Also, several nano-engineered magnetooptically active heterostructures (all-garnet multilayer-type thin film structures) based on magnetic layers with dissimilar uniaxial \((K_u > 0)\) and in-plane \((K_u < 0)\) magnetic anisotropies are prepared with the purpose of achieving the customised magnetic behaviour and properties (not attainable in single garnet layers) which are very attractive for the development of MO sensing devices and ultra-fast switches.
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CHAPTER 1

INTRODUCTION

1.1 Background

Garnets are a class of materials long used as gemstones or abrasives. Thin film garnet materials are important components for controlling and manipulating light waves thus making them very useful for various magneto-optical (MO) applications in integrated optics. The epitaxial growth of garnet thin films is of interest to researchers as garnet thin films can have high Faraday rotation and optical transmission in the visible and infrared spectral region. Bismuth substituted iron garnets (Bi:IG) are considered the best MO materials among all the rare-earth iron garnets. Bi:IG thin film material was first developed in 1960 for bubble memory device applications [1, 2]. Subsequently a number of research groups world-wide investigated their potential for integrated optics and photonics.

A large range of Bi-substituted iron garnet (Bi:IG) compounds, with compositions described by the generic formula (Bi, RE)₃(Fe, M)₅O₁₂, where RE stands for a rare-earth atom and M is a metal atom have been synthesized with high purity. Bi:IGs are particularly very appropriate for various multifunctional device applications including MO polarization control, latent marking, bank-note testing, light beam scanning, MO flaw detection, high-density MO data storage, and high-speed spatial light modulation, as well as magnetic photonic crystals (MPC) for the development of next-generation integrated devices [1-29]. Recently, several new structures for nanophotonic applications, based on Bi:IG thin film materials have been suggested and investigated, e.g. magnetic plasmonic heterostructures [2, 3, 11-20]. Bi-substituted iron garnets possess very high Faraday rotation in the visible light spectrum and relatively low optical absorption in the near infrared spectral region. However the high optical absorption losses across the visible spectral range and the absence of uniaxial magnetic anisotropy in sputtered high-bismuth-content garnet films (with compositions close to Bi₃Fe₅O₁₂) significantly limit the potential of Bi:IG materials for practical integrated-optics applications. Most garnet thin films with perpendicular magnetization \( \vec{M} \) possess high coercive force; however for some applications low-coercivity films are required. Low-coercivity films with either the in-plane-oriented easy axis of magnetization or
having a strong in-plane magnetization component along with very high MO quality are simultaneously required for several important applications such as waveguide-embedded polarisation control, magnetic field imaging and sensing devices. In integrated optics and photonics different applications require multiple variations in the properties of garnet materials, which can be engineered by adjusting the material composition.

The physical properties (optical, magnetic and MO), of all garnet materials required for any particular application, significantly depend on not only the Bi content and the substitution of other extra atoms and dopants within the sublattices of the garnet structure, but also on the multiple process parameters relevant to the synthesis of Bi:IGs [18]. Bi-substituted iron garnet thin film materials have been prepared and synthesized with different stoichiometry using various physical and chemical methods. The most common technologies used to fabricate garnet thin films of high surface quality, impurity-phase-free garnet-phase layers on various substrate types are Pulsed Laser Deposition (PLD), Liquid Phase Epitaxy (LPE), Ion Beam Sputtering (IBS), Reactive Ion Beam Sputtering (RIBS), metal organic chemical vapor deposition (MOCVD), sol-gel technique, RF magnetron sputtering (and other physical vapour deposition techniques) [13, 17-28].

The use of physical vapour deposition techniques leads initially to growing the amorphous-phase oxide mixes if sputtered below the crystallization temperature of any given garnet type, which do not possess any ferrimagnetic properties characteristic of Bi:IG. For high substrate temperatures (in excess of 500-600°C), the deposition processes can lead to growing the in-situ-crystallized or most often partially-crystallized (poly- or nanocrystalline) layers with the required garnet-type volume-averaged stoichiometry. These still require suitably-optimized post-deposition annealing processes for garnet phase formation. Finely optimized deposition processes using hot monocryalline garnet substrates which are very closely lattice-matched to the growing garnet layers have yielded epitaxial-quality garnet layer growth [20]. However all physical vapour deposition pathways, towards the Bi:IG synthesis, require complex and multi-parameter process optimizations at both deposition and annealing stages. This approach (using the RF magnetron sputtering technique) to garnet synthesis has the strongest potential for the practical use of this class of functional materials in photonic
integrated circuits, optical fibre components and other technologies linked to using micro-fabrication processes.

RF magnetron sputtering deposition followed by oven-annealing in air atmosphere is one of the most flexible approaches to synthesizing magneto-optic garnet materials, and is usually compatible with other material types and with various modern micro-fabrication technologies. It is important to note that this approach allows highly efficient and convenient engineering of garnet material properties through implementing the required variations in the chemical composition without having to redesign any principal synthesis pathways. This work is devoted to the synthesis and characterisation of highly Bi-substituted metal doped iron garnet thin films of composition type \((\text{Bi, Dy/Lu})_3(\text{Fe, Ga/Al})_5\text{O}_{12}\) featuring strong out-of-plane or in-plane magnetization components and improved optical and MO properties suitable for various applications in integrated optics and photonics.

### 1.2 Aim of this project

The substitution of rare-earth or other metal ions which enter either the dodecahedral or tetrahedral garnet-sublattice sites, allows engineering of the properties of garnets such as their refractive index, specific Faraday rotation, optical absorption and the magnetic properties thus providing a diversity of materials’ composition and properties. For example, Lacklison et al. developed garnets of single-crystal phase with high MO figure merit and low saturation magnetization suitable for magneto-optic devices, by substituting Bi atoms into the Yttrium Iron Garnet (YIG) material system [6]. Bi-substituted gadolinium iron garnet films of composition \(\text{Gd}_{1.57}\text{Bi}_{1.43}\text{Fe}_5\text{O}_{12}\) have also been prepared and it has been found that their crystallization temperature and Curie temperature depended on the number of bismuth (Bi) atoms per formula unit [7]. Integrating the functional MO garnet materials into photonic systems (called magneto-photonic crystals, MPC) and integrated optics devices provides novel functionalities for devices that perform in radio-frequency (RF), microwave, terahertz-wave and optical bands. Rapid progress in developing integrated devices for optical telecommunication systems and magnetic field sensors requires extensive research on functional MO garnet materials for incorporating the high-performance garnet thin films in integrated optics and photonics devices. Research interest in functional MO garnets, especially in the
new classes of Bi-substituted metal-doped iron garnets, has been renewed after an initial peak in 1970-1990.

The present study sought to establish new classes of Bi-substituted garnets in thin film form to address the issues such as the source of high optical absorption in the RF-sputtered films and the search for an optimal composition of garnets for improving their optical absorption, specific Faraday rotation, surface quality, microstructure quality, domain structures, and magnetic memory properties.

1.3 Scope of thesis

The objective of this work is to synthesize several classes of highly bismuth substituted iron garnet thin film materials and investigate their structural, optical, magnetic and magneto-optical properties. This research work involved several principal stages including the in-depth literature reviews, theoretical analyses and experimental investigations of different materials. The following structure of activities undertaken during the project can be outlined to reflect on the scope of this work:

(i) Selection of the potential subclasses of Bi-substituted iron garnets which can be used in magnetic photonic crystals as well as in other integrated photonic devices as functional magnetic materials.

(ii) Establishment of a highly repeatable technique (RF magnetron sputtering and co-sputtering processes) to achieve the fabrication of highly bismuth substituted iron garnet layers on various substrate types.

(iii) Optimization of the identified material-specific fabrication and high temperature annealing crystallization processes and their parameters for synthesizing highly Bi-substituted iron garnet thin films of high quality.

(iv) Establishment of a range of relevant material characterization techniques for generating important data on the optical, structural, magnetic and MO properties of the films synthesized. All characterization experiments were usually followed by the data analysis aimed at evaluating of annealing-
process effects on the various properties of these garnets. A short study of the crystallization kinetics of thin-film garnet materials was undertaken and this led to estimating some important kinetics related parameters.

(v) Evaluation of the potential usefulness of several material types studied for the various existing, emerging or forward-looking applications in integrated optics and photonics.

(vi) Fabrication of high-quality thin film nano-structures (of either single- or multilayer type using garnets and also other dielectric or metal layers within their structures) with a good degree of control over the deposition processes (thickness and refractive index) as well as the control over their magnetic behaviours.

(vii) The design and fabrication of several magneto-statically coupled all-garnet triple-layer structures containing magnetically dissimilar garnet layers with a goal to achieve special magnetic behaviour types. This approach was shown to lead towards achieving some very interesting magnetic switching behaviour in structures, which were not seen previously from using any individual magnetic-layer components of these structures.

(viii) Based on the findings identified throughout this research program, several suggestions and ideas are provided for further expanding the scope of this study, as well as for future work directions that may need to be undertaken in the fields relevant to this thesis.

1.4 Contribution of this thesis

New functional magneto-optic garnet materials are needed for modern optics and photonics applications. The synthesis of several new classes of MO materials, using the techniques of RF magnetron co-sputtering optimized during this work, is novel as are some of the techniques used to characterize the properties of various garnets prepared in thin film form. The main contributions of this thesis are:
• The work focused on the technologies relevant to the preparation of highly Bi-substituted metal-doped iron garnets in thin-film form and resulted in finding the optimized processes and process-related parameters for the synthesis of RF-sputtered nano-engineered garnet thin film materials.

• Experimental works were carried out to identify the optimized thermal processing (high-temperature annealing) regimes for multiple types of highly Bi-substituted iron garnets and garnet-oxide co-sputtered thin-film nanocomposites.

• Experimental works were carried out to characterize the various properties of garnets and garnet-oxide composite thin films.

• The optical, magnetic and MO properties obtained in the crystallized garnet samples synthesised at ECU labs were analysed in detail.

• The detailed design and performance simulations of magnetic photonic crystal (MPC) devices suitable for polarisation control applications were performed and a new operating principle suitable for controlling these MPC devices was proposed.

• Experimentally demonstrated the potential and functionality of the newly-developed classes of highly Bi-substituted iron garnets for use in various applications such as MO sensing and visualization.

1.5 Thesis layout

The remaining chapters of this thesis are arranged as follows. Chapter 2 introduces the structure and properties of thin film garnet materials including Bi-substituted iron garnet thin films and the techniques used for their fabrication. A background study related to the magneto-optical effects observed in garnet thin films and structures (single-layer and multilayer-type) is described in this chapter.

Thin film characterization is a key part of this research work as all of the garnet and garnet-bismuth oxide composite samples were prepared in thin-film form using RF
magnetron sputtering followed by high-temperature oven annealing crystallization processes. Chapter 3 presents a short description of some of the thin film characterization techniques which are commonly used for characterizing garnets and other dielectric materials. This chapter also briefly describes the techniques (experimental setups and processes) I applied to characterize the sputtered garnets and garnet-bismuth oxide nanocomposite-type thin-film materials.

Chapter 4 describes the fabrication techniques and process parameters used for growing two different types of highly Bi-substituted iron garnet thin films of compositions (BiDy)$_3$(FeGa)$_5$O$_{12}$ and (BiLu)$_3$(FeAl)$_5$O$_{12}$ which feature the magneto-hard (out-of-plane magnetization) and magneto-soft (almost in-plane magnetization) behaviours respectively. It introduces the concept of co-sputtering using the RF magnetron sputtering technique and an approach to synthesising garnet-bismuth oxide, nano-composite thin films. The optimized annealing processes for these classes of thin film garnet materials are also discussed. The effects of adding excess Bi$_2$O$_3$ content into the garnet-type layer volume during the co-sputtering processes, on the various properties of crystallized garnet materials are detailed in this chapter. The experimental results for optical, magnetic and MO properties of the typical garnet and the garnet-bismuth oxide composite materials are also detailed in this Chapter 4. The concept of all-garnet multilayer structures (sandwiching a garnet layer having an almost in-plane magnetization, in between two garnet layers having a perpendicular magnetization) used to engineer the magnetic properties of garnet material systems, and the experimental results (these achieved so far) are also included.

The effects of annealing crystallization treatment (crystallization temperature and process duration), on the properties of these types of garnet materials, are presented in Chapter 5. This chapter includes the details of an experimental study of isothermal annealing processes used for crystallizing the garnet-oxide composite thin films and the evaluation of the optical and magneto-optical properties of garnet films obtained. The crystallization kinetics details relevant to the garnet phase formation within a garnet-Bi-oxide nano-composite material type (Bi, Dy)$_3$(Fe, Ga)$_5$O$_{12}$: Bi$_2$O$_3$, are also discussed in this chapter.
Chapter 6 explores the potential of newly synthesized MO garnet materials for various applications in integrated optics and photonics such as MO isolators, magnetic field visualizers and spatial light modulators. The design of optimized nano-structured magnetic photonic crystals including the building blocks of MPC structures for use in magneto-optic polarization controllers at the communication-band wavelengths, the basic principle of MO visualization, and the MO modulators are also described in this chapter.

The final Chapter 7 summarises the major achievements of this study. The potential for further research on the development of functional magnetic materials, as well as for practical applications of these garnet materials in optics and integrated photonics is also explored.
CHAPTER 2

PROPERTIES OF GARNET MATERIALS AND TECHNIQUES USED FOR THEIR SYNTHESIS

Introduction

In this chapter, the various properties of garnet materials including the solid state structure of rare-earth doped garnets and some of their subclasses are discussed. Thin film preparation techniques (most commonly used ones), a background study and a short history of Bi-substituted iron garnets will also be presented.

2.1 Solid state structure of garnet materials

Garnets are a chemically diverse group that includes various silicate minerals. Menzer, in 1920’s documented the crystalline structures of silica-based garnets [30]. Subsequently, the characterization of ferrimagnetic garnets relied on the Neel theory of ferrimagnetism. The garnets are important to the technology used in modern electronic devices, however, the naturally occurring garnets have a limited utility. The synthesis of garnets and their structural refinement by including or doping a number of elements into the garnet system explored the scientific and technological benefit of garnets for various emerging applications in integrated optics and electronics [30, 31].

The crystallographic structure of garnet can be described using the general compositional formula \{C_3\}[A_2](D_3)O_{12} which represents a normal cubic structure of symmetry type \textit{Ia3d}, which comprises 24\{c\} dodecahedral sites with 8 oxygen neighbours, 16[a] octahedral sites with 6 oxygen neighbours, 24(d) tetrahedral sites with 4 oxygen neighbours, and 96 h-sites for oxygen ions. The most common and well known iron garnets are Yttrium Iron Garnet (YIG) and Bismuth Iron Garnet (BIG) can be chemically formulated as Y\textsubscript{3}[Fe\textsubscript{2}](Fe\textsubscript{3})O\textsubscript{12} and Bi\textsubscript{3}[Fe\textsubscript{2}](Fe\textsubscript{3})O\textsubscript{12} where Y\textsuperscript{3+} or Bi\textsuperscript{3+}
ions can occupy the dodecahedral sites, two of the Fe$^{3+}$ ions reside in octahedral sites and the remaining three Fe$^{3+}$ ions are in tetrahedral sublattice sites. Fig. 2.1 shows the solid state structure of rare-earth magnetic garnet materials.

The anti-ferromagnetic coupling of the octahedral and tetrahedral sub-lattices provides the ferrimagnetic properties of the crystals, in which the magnetic ions residing on dodecahedral sites are coupled weakly with the magnetic moments of the atoms residing on the tetrahedral sites. More details about the crystal structure of garnets are also available in Refs [2, 32]. The lattice constants for YIG and BIG are 12.38 Å and 12.63 Å respectively, while the lattice constant of a less common garnet of composition Bi$_3$Fe$_4$Ga$_1$O$_{12}$ (BIGG) is 12.61±0.01 Å, with the variation arising from the amount of gallium substitution [30, 32, 33]. Additional agents like gallium (Ga) and other dopants offer the preferential dilution of iron in octahedral and tetrahedral sites, thus reducing the net magnetization of the garnets. These types of garnets are very useful for various applications in integrated optics and photonics. In this thesis, the main emphasis has been to study several subclasses of garnet materials of the composition type Bi$_2$Dy$_1$Fe$_3$Ga$_1$O$_{12}$, Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$ and Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ by fabricating (Bi,Dy/Lu)$_3$(Fe,Ga/Al)$_5$O$_{12}$ garnets and also the novel garnet-Bi$_2$O$_3$ composites through using the RF magnetron sputtering technique. This sputtering procedure is very suitable
for integrating garnet thin films into optical devices. The presence of excess bismuth oxide content provides the improved transparency of films in the visible range, by forming an amorphous bismuth oxide-dominated matrix into which the garnet grains would be embedded after the crystallization process. The bismuth oxide (Bi$_2$O$_3$) target provides the source of extra Bi atoms to compensate for the possible loss of Bi content in the film or to even increase the Bi substitution beyond two atoms per formula unit. Specifically, the properties (optical, structural, magnetic, and MO) of RF sputtered, Bi/(Dy, Lu)-substituted (Ga/Al)-doped iron garnet composite films, containing different volumetric fractions of excess Bi$_2$O$_3$ co-sputtered from a separate target, have been investigated during this work. The combination of optical and MO properties achieved in these garnet materials, is very promising for use in microphotonic device development. This is especially the case for the manufacture of magnetic photonic crystal structures and other emerging MO applications including MO imaging and sensing, MO spatial light modulators, and garnet waveguides development.

2.2 The advantages of using functional garnet materials in thin film form

The most important advantage of thin film materials including garnets and other dielectrics is the ability to transform the materials’ properties to the film layers allowing the substrate and the thin film to form a material system that provides the functionality required for various applications and devices. Thin film technology allows achieving materials in thin film form with excellent electrical, optical, magnetic and magneto-optical properties and also provides significant controllability in terms of the films’ composition and other parameters. In many MO applications, the thin films must have the proper combination of properties such as high optical transparency and high MO performance to best exploit the potential of this nanoscale technology, single-crystal layers and heterostructures-type material systems are needed and these require the appropriate techniques and conditions for their deposition. Research and development into thin films has to address topics such as adhesion mechanisms between thin-film/substrates and between different layers, and the optimized equipment for fabrication and characterization.

Most of the garnet thin films of interest for various MO applications that have so far been fabricated using various deposition techniques are limited in their Bi substitution levels up to 1.2 – 1.5 Bi-atoms per formula unit. The ability to make high-quality garnet
multilayers can also be compromised by the thickness control issues often encountered with high growth rates (especially if liquid-phase crystal growth technologies are used). The RF-sputtered crystalline MO garnet films have some advantages over the thin garnet films prepared using other techniques as the sputtering technology allows depositing garnet thin films directly into the integrated devices as well as onto objects that need to be investigated. The deposition of thin films directly onto objects eliminates the object/film gap and maximises resolution if magnetic films are used for imaging. Studies of currents flowing in integrated current (IC) conductors are an example of this application [34]. Higher magneto-optic image contrast is also achievable by making spectrally-optimised nanostructures with high Bi doping levels, in magnetic layers.

2.3 Thin film preparation techniques

The deposition of the bulk material onto substrates at the nano level creates a thin film potentially with extra-ordinary material properties that may not be attainable using the substrate and bulk material alone. Thin films have a wide range of application areas, especially in the integrated-circuit industry, optical wave-guiding circuitry and also in micromechanical devices. Short descriptions of some of the more commonly used techniques for preparing thin films are given below.

2.3.1 Pulsed laser deposition (PLD)

PLD is a remarkable and simple technique for depositing thin films of different types of materials including semiconductors, and insulating and conducting metal oxides. A laser interacts with the target material and transfers energy into thermal, chemical, and mechanical energy in the material to be ablated. The deposition process can be described sequentially with the phases being ablation, plasma plume expansion and deposition onto the substrate, the layer nucleation, and the formation of film structure. Highly Bi-substituted YIG, BIG and also various Bi doped iron garnet films have been prepared using this technique [35-41]. PLD allows to deposit thin films with good material phase purity and also to preserve the target stoichiometry in the deposited films. However, it is difficult to produce a large area of uniform thin film and also protect the film surface from roughness due to particulates and molten droplets that adhere to the substrate.
### 2.3.2 Liquid phase epitaxy (LPE)

Liquid phase epitaxy (LPE) is the most extensively used technique for thin film deposition particularly for compound semiconductors and magnetic rare-earth iron garnets. This is a popular technique for depositing single (thick/thin) layer or multilayer garnet films with the high structural perfection and different stoichiometries needed for various integrated applications. It is a versatile growth technique for depositing thin films normally from either diluted solutions at low temperatures or from concentrated solutions. In general, diluted solutions are more preferable but due to the relatively high growth rate (0.1 to 1 µm/min), it is difficult to precisely control the film thickness which is critical to eliminate the linear birefringence. The growth rate of thin layers also depends on both the temperature and the composition of the solvents but it is challenging to control the target compositions. LPE is a scalable thin film deposition technique where multiple substrates can be possible to use to deposit thin films [42-49].

### 2.3.3 RF Magnetron Sputtering

RF magnetron sputtering is an enhanced method that allows thin film deposition at low operating pressure resulting in high quality thin films [19, 50-56]. The mechanism involves the ejection of atoms from the target material due to collisions with the sufficiently energised particles directed to the surface. This is one of the best physical vapour deposition processes developed to fabricate thin films materials and alloys through precise control of microstructure and phase. In the sputtering technique the substrate and the target material work as anode and cathode, respectively and the electrons are accelerated by the electric field between the substrate and target which ionize the Ar atoms to Ar⁺. Sputtering process is mainly conducted in four steps such as 1) ions are generated and directed at a target, 2) ions sputter targets’ atoms as a result of momentum transfer between the incident ions and the target materials, 3) the ejected atoms traverse the vacuum chamber and then 4) get condensed to form a thin film on the substrates. The sputtered atoms are deposited onto the substrates due to the bombardment of the target materials influence of the ionized gas atoms. The parameters related to thin film deposition onto the substrates using sputtering technology are RF power densities, target material stoichiometry and phase content, substrate temperature, distance between substrates & target, deposition time and the substrates stage placement geometry and rotation rate. Substrate cleaning and pre-sputtering are additional
processes required for high quality thin film deposition in sputtering process as pre-sputtering helps to bring the targets into stable sputtering conditions that can provide suitable deposition rates to produce thin films. A RF magnetron system (KVS-T 4065, Korea Vacuum Technology Ltd.) was used to prepare the Bi-substituted iron garnet and garnet-oxide composite films as shown in Fig. 2.2(a); Fig. 2.2(b) shows the schematic diagram of sputtering process. To adjust the level of doping agents for the garnet-oxide composite films the co-sputtering technique was implemented in this system using two separate targets at a time. This RF-magnetron technique is also very effective for the fabrication of thin film multilayers as well as nano-photonic crystals.
The sputtering procedure is very suitable for integrating Bi:IG films into optical components and devices allowing precise in-situ high-resolution thickness measurement due to relatively low growth rates. The film thicknesses can be monitored during the sputtering process with the in-situ laser reflectometry system. An s-polarized light is used to impinge on the middle of substrate during the thin film deposition and the reflected power is captured by the detector to measure the thickness of growing film,
using “Real-Time Thickness Control for Multilayers” software made at ECU. The film thicknesses can also be measured from the transmission spectra of pre- and post-annealed thin films. RF magnetron sputtered garnet thin films of different composition types are studied extensively by both researchers and innovative industrialists worldwide wishing to develop and also reconfigure integrated optics and photonics devices for practical applications.

2.4 Bi-substituted iron garnet films

The effect of interaction between the optics and magnetism simply called magneto-optics, provides a group of effects that are crucial for studying garnet thin film materials. A linearly polarized light wave which can be represented as the sum of two circularly-polarized waves with equal amplitudes, but opposite chiralities, which propagate with different speeds, and therefore a phase difference occurs between them, which is proportional to the path travelled [57, 58]. The well-known MO effects are Faraday effect and Kerr effect which are described in this section.

2.4.1 Faraday rotation

In 1845, the effects of interaction between light and a magnetic field were first observed by Michael Faraday and later became known as the Faraday effect, or Faraday rotation. Faraday rotation, a fundamental phenomenon in magneto-optics, is most commonly described as rotation of the plane of polarization of linearly polarized light. When the plane-polarised light passes through an optically transparent (or semi-transparent) medium and when a magnetic field is applied along the direction of light propagation, the light wave changes its polarisation direction, as shown in Fig. 2.3.
Fig. 2.3 Faraday effect; when plane-polarised light is passed through an optically transparent or semi-transparent MO medium and a magnetic field is applied along the direction of light propagation, the orientation of the polarisation plane of light is rotated (otherwise this effect can be described as magnetic circular birefringence).

The rotation angle is proportional to the magnitude of the applied magnetic field and also to the length (thickness) of the sample. The relationship can be defined as

$$\Theta_F = VBd,$$

where $B$ is the applied magnetic field strength, $d$ is the thickness of the substance through which the light is propagated and $V$ is the Verdet constant which varies with the wavelength and temperature.

In magnetic media, the Faraday effect is used to determine their magnetic hysteresis properties, to observe the magnetic domain structures, characterise the electronic energy level structure, and the details of their magnetization processes. These studies require samples transparent in certain frequency bands, or thin single-crystal sections of sufficient purity and perfection, or materials fabricated in thin film form. The Faraday effect magnitude observed in every particular material is an important parameter in magnetic media characterisation, particularly for applications in optical polarisation rotators, devices for power or amplitude modulation of light, remote sensing of magnetic fields, spin-wave magneto-optical electronics, and spintronics research. Multiple studies have been conducted to explain the Faraday effect theoretically and
experimentally and use this effect in different media with different modes of measurement. [59-64].

2.4.2 Kerr effect

Kerr rotation (Kerr effect) is an important property of MO thin film materials which is widely used in modern information processing technologies. Kerr rotation measures the changes of light reflected (both the state of polarization and the intensity of reflection light) associated with the magnetized media. Four types of magneto-optic Kerr effect (MOKE) such as Polar MOKE, Longitudinal MOKE, Transversal MOKE and Quadratic MOKE are usually defined based on the direction of the magnetization vector, with respect to the reflecting surface and the plane of incidence. High Kerr rotation allows a better signal-to-noise ratio which is very essential for magneto-optic storage media such as high density MO disks. Researchers have investigated the Kerr effect in thin film garnet materials including Bi-substituted iron garnet and also in magneto-photonic crystals as well as multilayer thin film structures [65-71].

Recently, Vladimir Belotelov and his research group have observed enhanced TMOKE in transmission mode in the garnet films of composition type Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ (prepared at ESRI, ECU by me) by using plasmonic nanostructures placed on top of the garnet films and also using our garnet-oxide composite films. This confirmed their theoretical predictions related to the enhancement of MO effects occurring through the excitation of surface plasmon polaritons [72, 73].

2.5 Optical and magneto-optical properties of bismuth substituted iron garnets

In magneto-optics, the yttrium iron garnet (YIG) and bismuth iron garnet (BIG) are the most common and well-known materials to be used in various applications. However, the improvements in material properties and their stability required for integrated optics and photonics have caused researchers to refine YIG and BIG to develop new thin film garnet materials. Specifically, the excellent Faraday rotation, and significant transparency of Bi-substituted rare earth iron garnet thin films have encouraged researchers to develop new garnets material with high bismuth substitution. The assumption is that bismuth ions are diamagnetic like the yttrium ions and they don’t
make any major change in the magnetic and dynamic characteristics of YIG, if yttrium is replaced by bismuth in the dodecahedral site of the garnet structure. However, in the structure of Bi-substituted iron garnet Bi are not likely diamagnetic, and their saturation magnetization and ferromagnetic resonance linewidth depend on the preparation techniques. It was then realized that bismuth doping strongly enhanced the magneto-optical Faraday rotation (FR) in iron garnets by about 2 deg/µm per every Bi-atom per chemical formula unit, when measured at 633 nm [74].

Bi-substituted iron garnets are not frequently used in visible range magneto-optics due to their high optical loss in the visible spectral region. However, excellent optical and magneto-optical properties of Bi-substituted iron garnet thin films, of various composition prepared using different technologies, have been reported by many groups [11, 15, 16, 24-27, 29, 40, 74 - 76]. Bi:IG films with high bismuth substitution (in excess of 1.5 Bi atoms per formula unit) have been produced using different techniques including RF magnetron sputtering, ion beam sputtering and pulsed laser deposition (PLD). They typically show very high optical absorption coefficients ranging between 3-5×10³ cm⁻¹ at 633 nm [16, 17]. Zhang et al. prepared Bi-substituted dysprosium iron garnet films by a sol-gel process, which possessed the perpendicular magnetic anisotropy and strong coercivity, but had a very low figure of merit [26]. Bi-doped iron garnet films of the composition type Bi₂₀Dy₁₀Fe₃₅Ga₁₀O₁₂, deposited by a laser ablation technique demonstrated perpendicular magnetic anisotropy and featured a square hysteresis loop and 0.78°/µm of Faraday rotation at 628 nm at the remanent state of magnetization [29, 74]. (BiY)₃Fe₅O₁₂ films on Nd₃Ga₅O₁₂ substrates prepared by Ion Beam Sputtering (IBS) technique possessed a specific Faraday rotation of Θ_F = - 5.5 deg/µm, [75] and a bulk single crystal layer of (BiYbY)₃(FeGa)₅O₁₂ were prepared to improve the sensitivity constant, and temperature dependence of iron garnets for optical current/magnetic field sensors through this compositional modification and found comparatively higher magnetic-filed sensitivity than that of pure YIG [59]. Also, Bi-substituted mixed rare-earth iron garnet crystals of composition type Tb₃+−xYbₓBiₓFe₅O₁₂ have been synthesized, and these demonstrated small specific Faraday rotations which were however useful for designing bulk-optic isolators for broadband optical communications [76].
Kahl et al. first reported in 2001 on completely Bi substituted $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ garnet films prepared by the pulsed laser deposition (PLD) technique that possessed in plane magnetization with a high Faraday rotation angle of up to 7.8 deg/$\mu$m (measured at 633 nm). The maximum specific Faraday rotation reported so far in $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ was about $\Theta_F = -8.09^\circ/\mu$m at 633 nm. Also, BIGG ($\text{Bi}_3\text{Fe}_4\text{Ga}_1\text{O}_{12}$) films have been prepared for ultrafast switching applications by using the PLD technique and demonstrated a MO figure of merit of $(16.5^\circ\pm1^\circ)$ at 532 nm [23, 33, 77, 78].

$\text{Bi:IG}$ films often deviate from their nominal stoichiometric composition because of the various factors which affect the deposition process. For example, $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ films produced by RF sputtering are likely to have excessive iron and iron oxide(s) content, and a further loss of bismuth and bismuth oxide content can occur during both the deposition and annealing processes. The latter is due to the elevated saturated vapour pressure of these compounds compared to other oxides. Since the iron oxides demonstrate a high optical absorption in the visible range, the presence of excess $\text{Fe}_2\text{O}_3$ or $\text{Fe}_3\text{O}_4$ phases residing outside the garnet grains (nanocrystallites) can dramatically increase the absorption losses in RF-sputtered doped iron garnet films. Bearing in mind that the presence of excess iron oxide phases is largely responsible for the high absorption of sputtered garnet films (when compared to epitaxially-grown monocry stalline garnet layers), in this study several batches of co-sputtered garnet-bismuth oxide thin film composites were fabricated using two types of base garnet targets having different magnetic behaviour (out-of-plane magnetization and almost in-plane magnetization vector direction) with a separate $\text{Bi}_2\text{O}_3$ target. The properties of these films were investigated optically, magnetically and magneto-optically using a set of thin film characterization technologies employed frequently in this research work. The presence of excess bismuth oxide content provides the improved transparency of films in the visible range, by forming an amorphous bismuth oxide-dominated matrix into which the garnet grains would be embedded after the crystallization process. Another purpose of adding the excess $\text{Bi}_2\text{O}_3$ was to provide an additional source of Bi atoms and therefore compensate for the possible loss of Bi content in the film, or to even increase the Bi substitution beyond two atoms per formula unit.

The results obtained with these composite films (discussed in Chapter 4) suggest that the goal of achieving highly Bi-substituted (up to 2 Bismuth atoms per formula unit)
iron garnet thin films with extra-ordinary material properties, which make them very attractive for use in nano-structured magneto-photonic components and devices, have indeed been achieved.

2.6 Magnetic multilayer thin films and magneto photonic crystals (MPC)

There are many devices in integrated optics and photonics that rely on the functionality of the Faraday effect. Sometimes they also require very special MO features which can be achieved by designing an optimized thin film (single layer or multilayer). The Faraday rotation can be engineered at a chosen wavelength by making different types of multilayer structures including magnetic photonic crystal (MPC), all garnet multilayer structures, and sandwiching of MO layers between highly reflective and wavelength selective dielectric materials [79-81]. Many different types of 1-D MPC structures and multilayer garnet and all-garnet heterostructures have been proposed and developed to enhance the MO properties, mainly the Faraday rotation and Kerr rotation. However, in practice, it is very challenging to have such multilayer thin film structures (having garnets and dielectric layers with either periodic or non-periodic structuring) with simultaneously high Faraday rotation and high optical transmission [82]. A MPC structure can predict almost 100% wide-band optical transmission and about 45º of Faraday rotation at 1550 nm using cerium-substituted yttrium iron garnet (Ce:YIG) and gadolinium gallium garnet (GGG) layers in a complex film of total thickness 35-40 µm [83]. The maximum Faraday rotation angles measured for an all-garnet heteroepitaxial MPCs were about 20.06º at 750 nm and 8.4º at 980 nm, as reported in [84].

However, in practice these structures are of significant complexity and are very challenging to manufacture, and also to integrate on-chip. But the RF magnetron sputtering process allows controlling the thin films quality and offers the flexibility to integrate the Bi:IG films into optical devices with precise in situ high-resolution thickness measurement due to relatively slow growth rates. The properties of garnet thin films together with the advantages of their fabrication technology can be very attractive for various device applications (especially when fabricating single-layer structures sputtered onto parts of the chip or integrated device) in telecommunication and information technology.
Several MPC structures, capable of demonstrating very large Faraday rotation angles at the communication-band wavelengths, have also been designed during the course of this study. The designs of MPC structures have been generated using the materials characterization data obtained from Bi-substituted Ga-doped dysprosium iron garnet layers, fabricated using RF magnetron technology, followed by high temperature oven annealing crystallization. The design parameters and the performance outcomes (optical transmission and Faraday rotation angle) of the optimized nano-structured MPCs (designed) are described in Chapter 6. Several all-garnet multilayer thin films (3-5 layers) containing magnetic and paramagnetic layers, have been sputtered and processed through optimized annealing crystallization regimes to characterise the precision of making MPCs as well as multilayers thin films up to several micron thick onto different substrate types. Some were characterized fully, and some are still characterized only partially, and the best achieved performance characteristics of these multilayer thin films are detailed in Chapter 4.

### 2.7 Summary

The background information on garnet materials and their magneto-optic properties has been described in this chapter. Several technologies used for the fabrication of thin film garnet materials including RF magnetron sputtering have also been discussed. The techniques for thin film garnet characterization and the techniques used in this work to characterize and test Bi-substituted iron garnets and garnet-bismuth oxide composite thin films will be described in more detail in Chapter 3.


**Chapter 3**

TECHNIQUES FOR THE MANUFACTURE AND CHARACTERIZATION OF MO THIN FILMS

**Introduction**

Characterization of thin films involves investigating the materials properties such as the crystallinity of layers grown on various substrates, film layer thickness, magnetic domain structures, and the optical, magnetic and magneto-optic properties. The techniques used in general to characterize the properties of thin film materials including garnet materials are described in this chapter, however it was not possible to apply all techniques in my work as some of the technological constraints were limiting the scope of this study.

3.1 **Crystal structure**

3.1.1 **X-ray diffraction method (XRD)**

X-ray diffraction (XRD) measurement is one of the most accurate and general methods used to characterize and investigate the growth quality and microscopic properties, such as crystal structure, crystal orientation, and the crystal deformation of thin films as well as the existence of any preferential orientation (texture) within the film crystallites and its dependency on substrate. XRD is also applicable to determine the residual stresses produced by surface treatments of polycrystalline materials, enabling high spatial resolution to a wide variety of sample geometries. This is a non-destructive method and can be carried out under different measurement conditions to investigate the materials properties, useful to develop new materials [34, 85-89]. X-ray diffractometry helps to determine the spacing between layers or rows of atoms, size, shape and internal stress of small crystalline regions, eventually the crystalline structure, and the lattice parameter if performed with a specific wavelength of x-ray. This method is based on Bragg’s diffraction law (Fig. 3.1) which can be expressed mathematically as follows:

\[ 2d \sin \Theta = n \lambda \]

where \( \Theta = \frac{1}{2}(2\theta) \), and \( d \) is the spacing between the lattice planes which is perpendicular to the wavevectors of incident and diffracted radiations \( K-K' \) satisfying the relation \( K-K'=G \), where \( G \) is the reciprocal lattice vector.
The diffraction patterns consist of different reflection intensities (generated by coherent and elastic scattering) of light, from which the crystal structure is determined. And the reflection maxima in the diffraction pattern represent the Bragg peaks.

![Diagram of the Bragg's diffraction law](image)

**Fig. 3.1** The geometric structure of the Bragg’s diffraction law; the incident light rays of identical wavelength scatter off two different atoms within the crystalline solid and an extra path (2d sin Θ) is travelled by the lower beam.

The crystal structures and the phase content of various garnet-type thin film materials including Bi-substituted iron garnets having different Bi-contents have been determined using X-ray diffraction measurements [40, 53, 55, 90-94]. A Panalytical Xpert Pro X-ray diffractometer was used to characterize the crystalline structure of my garnets and garnet-oxide composite layers prepared on different substrates. These X-ray diffraction measurements were carried out at the Materials Characterization Lab in Korea Optical Technology Institute (KOPTI, Gwangju, South Korea). A Θ - 2Θ scan (with a wide angle range of between 20 - 80 degrees) was performed for all the garnet samples to find the crystalline orientations as well as the lattice constant of highly Bi-substituted iron garnet and garnet-oxide composite materials of composition type (BiDy)₃(FeGa)₅O₁₂. Fig. 3.2 shows the X-ray diffraction patterns obtained in optimally annealed typical garnet and garnet-oxide composite films.
3.1.2 Energy dispersive X-ray spectroscopy (EDX or EDS)

Energy Dispersive X-ray Spectroscopy (EDX or EDS) is an analytical technique that is used in conjunction with scanning electron microscopy (SEM) to determine the structural properties and the elemental composition of the films. In this technique, the detector measures the X-ray wavelength and power emitted from the sample, which occurs during the bombardment of sample by an electron beam [94, 95]. In this work, EDX measurements were performed to confirm the presence of all elements expected to be present within the garnet films, and the experiments were carried out at the Gwangju Institute of Science and Technology (GIST) characterization labs.

3.1.3 Auger electron spectroscopy (AES)

Auger electron spectroscopy is a surface science technique and very useful to measure the stoichiometry of thin films, as well as the top few layers of a surface and the interface of multilayer structures. However it requires special sample preparation and ultra-high-vacuum (UHV) annealing processes [95, 96]. In this technique the Auger electrons (ejected due to the interaction between the sample and electron beam) exit the
sample surface and are used to collect the elemental information about the sample surface. AES is a very sensitive technique to analyse the surface of the films with high spatial resolution.

3.2 Thickness measurements and fitting

In thin film technology, it is very important to measure and control the film thicknesses very precisely as the properties of thin film materials are dependent on the film thicknesses. There are several ways to control the film thicknesses during the deposition process and also remeasure the film thicknesses after the deposition.

3.2.1 Profilometry

Profilometry is a mechanical method used to determine the thin film thicknesses. This technique requires a special process of thin film formation to determine the film thicknesses which also requires the presence of a groove between the substrate and the film surface [97].

3.2.2 Reflectometry

Reflectometry is used to monitor the thin film thicknesses during the deposition based on the power of a laser beam reflected from the film–substrate system. The light reflected from the film produces intensity oscillations due to the interference fringes caused by the growth of thin films on the substrates, and the reflected power is captured and measured to calculate the film growth rate and the thickness of the film. This method is preferable to other techniques because it is not affected by radio-frequency noise (unlike quartz crystal microbalances), and also it is possible to compare the growth rate, and the refractive index of the thin film with the modelled results [97]. This technique was used in my research work to monitor the film thicknesses during the garnets layers deposition. The film thicknesses were calculated from the reflected power dependencies using specialised software package “Real-time thickness control for multilayers” (ECU-fabricated software, written by Dr. Mikhail Vasiliev in 2007). This is one of the most reliable and frequently-used thickness measurement techniques utilised during this work.
3.2.3 Scanning Probe Microscopy (SPM) for characterization of film topography

Scanning probe microscopy is a powerful research tool that allows imaging and characterisation of thin film surfaces on a fine scale, down to the level of molecules, and groups of atoms. The sample surface is examined by an atomically sharp cantilever tip (3-50 nm radius of curvature) scan performed over the film surface whilst using an electronic and also mechanical feedback mechanism. The cantilever tip maintains a constant force or height above the surface while scanning of the sample is performed in the nano-scale resolutions range. This scanning mechanism detects nano-scale increments in the x, y and z directions and enables to acquire three-dimensional images of sample surfaces. There are three commonly-used scanning techniques such as contact mode, non-contact mode and semi-contact (tapping) mode that can be used to investigate the thin film surface and from the scan data, the surface roughness of films and in some cases, the film thickness can be determined. Scanning probe microscopy covers several related technologies and the most common scanning probe techniques are atomic force microscopy (AFM) that measures the interaction force between the tip and sample surface, scanning tunnelling microscopy (STM) which measures a weak electrical current flowing between the tip and sample, and scanning near-field optical microscopy (SNOM) that can scan with a very small light source placed very close to the sample which forms the topography image.

3.3 Thin Film morphology measurements

3.3.1 Atomic force microscopy (AFM)/Magnetic force microscopy (MFM)

The surface morphology and the surface magnetic field distribution topography of garnet films can be characterized using atomic force microscopy (AFM) and magnetic force microscopy (MFM). These are very useful techniques to obtain high-resolution images of thin film surfaces in the order of fractions of a nanometer. Fig. 3.3 shows the results of surface quality inspection performed in a typical Bi-substituted iron garnet films of 4 µm thickness, and the obtained RMS surface roughness of the garnet layer was about 2 nm across a randomly-selected film area of 1 µm².
Fig. 3.3 AFM image obtained from an annealed 4 µm thick Bi-substituted iron garnet layer shows high surface quality of the thin film material [19]. This AFM image is courtesy of Young Min Song, Gwangju Institute of Science and Technology, South Korea.

Also a magnetic force microscope (NT-MDT Nova Scanning Probe Nanolaboratory, shown in Fig. 3.4) was used to observe the film morphology and the main magnetization vector directions across the garnet film surfaces in films of composition type (BiLu)₃(FeAl)₅O₁₂. The garnet samples were scanned using semi-contact mode of probe-interaction to obtain the two-dimensional feedback-phase and also the surface topography data simultaneously from the same scan area. The MFM cantilever tip used was cobalt-coated to enable the magnetic-force interaction representation through the phase of the cantilever feedback signal. The magnetic domains structure and the map of magnetic interaction force between the cantilever tip and sample surface could also be imaged.
The film morphology also can be investigated by using the scanning electron microscope (SEM) which is a flexible and versatile instrument, and it was possible to scan and observe surface features and also bulk cross-sections in garnet samples of several microns thickness, if these had a top silver coating (10-15 nm) sputtered onto garnet samples to provide electric conductivity.

Some other techniques such as Rutherford backscattering (RBS) and transmission electron microscope (TEM) imaging, are also used to determine the materials distribution within samples and the internal microstructure including the morphology and material phases within the films.

### 3.4 Optical characterization

The optical properties of thin films such as absorption, transmission and reflection spectra, electronic band-gap properties, spectra of refractive index and extinction coefficients can be determined using the following characterization techniques.

#### 3.4.1 Ellipsometry

Ellipsometry is a very common and useful technique for measuring the thickness, refractive index, and the extinction coefficients of thin films as well as the bulk materials. This technique is in general based on how the components of polarized light
(P- and S- polarised electric field components) get changed due to the reflection from
the sample surface, and the changes in light polarisation (comparison between the input
and output signal called the ratio of Fresnel reflection coefficients) are measured to
extract the information about the thickness and refractive index of thin film materials.
This process is highly sensitive and non-destructive but it can be quite complex to apply
and analyse in thick samples of several microns thickness. This technique is used
widely in electronics and materials science [97-99].

3.4.2 Spectrophotometry

Spectrophotometry is used to measure the light intensity of transmitted light passing
through the sample as a function of wavelength. A photo-detector captures the intensity
of the transmitted light to analyse and characterize the transmission and absorption
coefficients of thin film materials. The theory of spectrophotometry measurement is
based on the relationship between the absorption and transmission coefficients which is
usually defined by the following expression (3.2).

\[ A = - \log T \]  \hspace{1cm} (3.2)

where \( T = \frac{I}{I_0} \), is the ratio of transmitted light intensity \( I \) to that of the incidence light
\( I_0 \) [100].

A Beckman Coulter DU 640B UV/Visible spectrophotometer was used in this work to
obtain the transmission spectra in typical garnet layers as well as in garnet-oxide
composite layers, and the measurement set-up is shown in Fig. 3.5 with a schematic
diagram of sample chamber and measurement process. It is easy to calibrate the system
by making a blank transmission spectrum without any sample before performing the
transmission measurement of the sample. When the light passes through the sample, a
certain amount of light is absorbed and some light is reflected by the sample (and in
some samples, some light is also scattered by the film layers), and the remaining power
of the incident light is captured as transmitted light for spectral analysis.
In this research work transmission spectra measurement for all the batches of garnet and garnet-oxide composite layers (as-deposited and annealed) were one of the important tasks as the physical layer thicknesses and the absorption coefficients of garnet thin film materials were derived using the obtained transmission spectra by the spectrophotometer to the specialized thickness-fitting software. Fig 3.6 shows a comparison of the measured transmission spectrum of a garnet (BiDy)$_3$(FeGa)$_5$O$_{12}$ film on a GGG substrate (blue line) and its modeled transmission spectrum (red line), where the material’s refractive index dispersion function has been measured and fully accounted for in the model.
Fig. 3.6 Modeled (red line) and measured (blue line) transmission spectrum of a Bi$_3$Dy$_1$Fe$_3$Ga$_4$O$_{12}$ garnet film prepared on a GGG (111) substrate [19].

The fitting of the actual films’ thickness for all garnet films fabricated were performed by closely matching the measured transmission spectrum features to the modeled spectrum. The modeled transmission spectra for all the garnet and garnet-oxide thin films were calculated using the 4x4 transfer matrix method, using which the predicted Faraday rotation spectra (computed using the spectral dependencies of all complex-valued dielectric tensor components) were also calculated [101].

3.5 Magnetic and magneto-optical characterization

The properties such as magnetic domain structure, saturation magnetization, magneto-optic Kerr effect magnitude, specific Faraday rotation, MO figure of merit and hysteresis loop of Faraday rotation are the most important properties to investigate in thin film garnet materials. The domain structure observations and the measurements of Faraday rotation spectra and also the hysteresis loops of Faraday rotation were performed during this research work.

3.5.1 Vibrating Sample Magnetometry (VSM)

VSM is the method used to determine the magnetic properties by measuring the magnetic moment of the sample with high accuracy. This method is based on the Faraday law of induction and the measurements can be performed using externally-generated magnetic fields. In this measurement technique, the sample is usually placed
between a pair of pick-up coils at the end of a rigid rod attached to a mechanical resonator. The sample gets the oscillation at a fixed vibration frequency in the vertical direction provides by the lock in amplifier which also detect the signal of changes in magnetic flux through the coils to analyse the sample properties. It is also possible to measure the hysteresis loops of thick films [89, 102, 103]. But the vibrating sample magnetometer is not suitable for measuring the magnetization of single-layer iron garnet thin films on GGG substrates because the signal from thick paramagnetic GGG substrates is much higher than that obtained from the garnet films.

3.5.2 Faraday rotation angle and MO figure of merit

The interaction between light and media that is well known as Faraday rotation is a magneto-optical phenomenon and can be expressed mathematically by the following equation:

\[
\Theta_F = \frac{\theta_t - \theta_s}{d}
\]  

(3.3)

Where \( \Theta_F \) is the total Faraday rotation measured for the combined film and substrate system, \( \theta_s \) is Faraday rotation of the bare substrate, and \( d \) is the film thickness. The Faraday rotation per film thickness of all the batches of garnet and garnet-oxide composite thin films was measured (after annealing) across the visible spectral range. The set-up used for both the Faraday rotation and the hysteresis loop of Faraday rotation measurements is shown in Fig. 3.7. It is also possible to determine the Faraday rotation spectra in garnet thin films by considering the character of diamagnetic electronic transitions (one related to a tetrahedral and one to an octahedral site), as was described theoretically and confirmed experimentally in [88, 104].

The magneto-optic quality factor (MO figure of merit), which is defined by the ratio of the doubled specific Faraday rotation to the material absorption coefficient at each wavelength, was calculated using the measured Faraday rotation data. This definition can simply be expressed as follows

\[
Q = \frac{2\Theta_F}{\alpha}
\]  

(3.4)
where $\Theta_F$ is specific Faraday rotation measured in films at the saturated (or sometimes, remnant) magnetization state and $\alpha$ is the optical absorption coefficient measured at the same wavelength. MO figure of merit allows comparing the expected performance of new or existing materials quickly and quantitatively which is very important and essential in new MO materials development for magneto-optic device applications [105, 106].

Fig. 3.7 Schematic of the set-up of Faraday rotation and Faraday rotation hysteresis loop measurement system used in this work to characterize the garnet films.

This measurement system is based on using linearly polarized laser light sources (mostly the sources working in the visible spectral range). The experimental setup contains a custom-made well-calibrated electromagnet and also a Thorlabs PAX series polarimeter to characterize the garnet thin films. The calibration accuracy of the Thorlabs PAX polarimeter (used for Faraday rotation measurements) was confirmed by using two experimental setups, (i) the direct measurements of optical power transmitted through the sample and the use of an analyzer rotated 45 degrees with respect to the polarisation direction of the incident laser light, under various magnetization conditions, and (ii) a well-calibrated measurement setup based on the detection of polarisation components. The measured Faraday rotations for both setups were in excellent agreement. The Thorlabs PAX polarimeter had a high dynamic range of 70 dB, a broad wavelength range, and an absolute accuracy of $\pm 0.2^\circ$. The sample to be characterized is
usually placed into the middle of electromagnet gap and the polarized light is allowed to pass through the semitransparent garnet thin films along the direction of external magnetic field applied.

3.5.3 Hysteresis loop measurement

Magnetic hysteresis loop is the relationship between the magnetic flux induced within a magnetised material and the external magnetic field strength variations, which allows characterisation of the magnetic switching behaviour and the confirmation of the uniaxial magnetic anisotropy type of garnet thin films. Hysteresis loop measurements in garnet and garnet-oxide composite thin films were performed using the same setup as shown in Fig. 3.7 in the materials characterization lab at the Electron Science Research Institute in Edith Cowan University. The measurements of hysteresis loops of Faraday rotation in garnet thin films were performed in the presence of external magnetic field applied in the direction perpendicular to the film plane and parallel to the light propagation direction.

3.6 Magneto-optical imaging and magnetic domain structures

3.6.1 Optical microscopy

A polarization microscope can be used to observe the magnetic domain patterns of thin film magneto-optic garnet materials. In this work a transmission-mode polarization microscope (Leitz Orthoplan, as shown in Fig 3.8) was used to observe the magnetic domain patterns of Bi-substituted iron garnet films.
The domain structures of the garnets and garnet-oxide composite thin films were observed in the absence of external magnetic fields, in demagnetised samples. This technique was also applied for magneto-optic imaging to observe the magnetic patterns recorded into the various magnetic storage media. Fig. 3.9 shows the magnetic domain patterns obtained in a high quality multilayer structure and also a MO image of HD floppy disks’ data patterns recorded onto a garnet thin film by way of “imprint magnetisation” which transferred the magnetisation distribution pattern from the diskette surface onto the garnet film surface. The garnet films having uniaxial magnetic anisotropy memorise the images of data patterns after a brief mechanical contact with the floppy disk surface.
Fig. 3.9 Magnetic domain pattern obtained using the Leitz Orthoplan polarization microscope in a high quality multilayer thin film heterostructure sputtered onto GGG; (b) Image of HD (1.44Mb) floppy disk’s recorded patterns on a garnet thin film of composition Bi₂Dy₁₄Fe₄.₃Ga₀.₇O₁₂ prepared on GGG (111) substrate.

3.7 Summary

Thin film characterization has been a key part of this research work. Various techniques of thin film characterization have been discussed including those used to characterize and investigate the properties of highly Bi-substituted iron garnet and garnet-oxide composite thin film materials. The experimental processes, for garnet thin film materials characterization, used in this research work to investigate the properties of thin film garnet materials, are also partially discussed in this chapter. The fabrication processes as well as the optimization of process parameters of Bi-substituted iron garnets and their nano-composite derivatives also obtained in thin-film form, and their characterization results are detailed in the next chapter.
CHAPTER 4

RF MAGNETRON SPUTTERED HIGHLY BI-SUBSTITUTED IRON GARNET FILMS

Introduction

Several important classes of highly Bi-substituted iron garnet thin-film materials have been prepared and characterized in terms of their optical, magnetic and magneto-optical properties. This chapter also introduces the concept of co-sputtering garnet-bismuth oxide composite films by adding an optimized amount of excess oxide from a separate Bi$_2$O$_3$ target during the deposition process. All the garnet-bismuth oxide composite films were subjected to a high temperature annealing process to crystallize the initially-formed amorphous-phase layers. The best results obtained with the nanocomposite films in relation to the typical garnet film properties are discussed in this chapter.

4.1 Film synthesis and thermal post-processing parameters

4.1.1 Thin film growth

Bi-substituted garnet and garnet-oxide composite (having 4-50 vol. % of excess Bi$_2$O$_3$ content, as measured in relation to each corresponding garnet composition stoichiometry, and represented in this way due to using oxide-mix-based sputtering targets which also contain some bismuth oxide) amorphous-phase films were prepared by RF magnetron sputtering onto different substrate types such as Corning 1737, Corning Eagle XG, microscope slide glass of various types, polished monocrystalline GGG (111), and Silicon (Si). Low-pressure pure-argon plasma was used to bombard the target materials and enhance the sputter deposition rate. Several batches of garnet and garnet-oxide composite thin films were prepared using a range of substrates’ temperatures between 250-800 °C during the deposition processes. It was found that the substrate temperature of 250 °C was suitable for most of the garnet and garnet-bismuth oxide composite films deposition and no composite garnet films were deposited using a higher temperature than 250 °C. The substrates used to prepare the thin films were
always ultrasonically cleaned using acetone, isopropanol and deionized water. Before the deposition of thin films, some precautions were always taken such as pre-sputtering of the targets for 10-30 minutes to bring them into stable deposition conditions, the rate of substrates stage rotation was set up to 50 rpm to ensure the uniform deposition of thin films, the argon flow rate and partial pressure were fixed, and the reference value was taken for the measurement-beam optical power reflected from the bare substrate to monitor the growing film thickness. A Newport power meter (Model 2931-C) was used in the custom made in-situ reflectrometry system to receive the reflected laser power from the sample during the deposition of thin films.

A schematic diagram of the co-sputtering geometry used is shown in Fig.4.1 (up to two guns were used concurrently in my experiments). The target materials (garnet and bismuth oxide) of 3” diameter were placed at three RF guns of the down-sputtering system (KVS-T4065; Korea Vacuum Technology Ltd) having about 18 cm of source-to-substrate separation. All the guns with independently-activated gun shutters were placed at the corners of an equilateral triangle and tilted towards the substrates. In the co-sputtering technique, the Bi₂O₃ target was used as the additional source of Bi atoms to compensate for either the possible loss of, or even to achieve an increase in, the Bi content in the films beyond two atoms per formula unit.

![Diagram](image_url)

**Fig. 4.1** (a) Schematic diagram of the co-sputtering system geometry and (b) flow chart of the processing of garnet-bismuth oxide co-sputtered thin films.
4.1.2 Oven-annealing heat treatment

Conventional temperature/ramp-controlled box furnace ovens were used to anneal the as-deposited (amorphous) garnet layers to produce the polycrystalline (micro- or nanocrystalline) garnet phase in air-atmosphere. The post-deposition annealing treatment primarily allows the softening of the materials and simultaneously producing the desired changes in microstructure and other properties of the sputtered amorphous garnet films. The annealing heat treatment of thin films is a sequence of three process steps as shown in Fig. 4.2. The first step consists of heating to the recommended annealing temperature using a temperature ramp-up process, the second step is holding the suitable temperature for a specified annealing time for isothermal crystallization, and the last step is cooling at the same temperature-ramp rate. The annealing processes were run using optimized crystallization temperatures and time regimes for each particular stoichiometry type of the garnet materials. The annealing process durations of up to 10 hours have been used with temperature-ramp process rates of 3-5 °C/min to crystallize the amorphous (as-deposited) layers into a high-quality nanocrystalline garnet phase with relatively small grain size.

![Diagram of annealing process](image)

Fig. 4.2 Schematic diagram of the annealing processes run in order to crystallize the garnet layers with the conventional box-furnace-type oven annealing system.

The annealing process with the low temperature-ramp rates were preferred to crystallize the amorphous garnet layers as, in my experience, garnet films annealed with the rapid thermal annealing process were subject to micro-cracks and surface damage. The optimization of annealing regimes (temperature and annealing process duration) was found to be completely composition dependent and the optical and MO properties of
garnet thin film materials are critically related to the optimization of annealing of garnet materials [19]. The optimized annealing temperature regimes for the typical (BiDy)$_3$(FeGa)$_5$O$_{12}$ garnet layers were observed to be within the range of about 580-700°C, and temperatures between 480-620°C were used for (BiDy)$_3$(FeGa)$_5$O$_{12}$ :Bi$_2$O$_3$ composite layers; typical durations of crystallisation process were between 30-60 minutes. The annealing processes were run for the typical Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ layers using temperatures in the range of 620-700°C, while the temperature range of between 610-620°C was found suitable for the (BiLu)$_3$(FeAl)$_5$O$_{12}$: Bi$_2$O$_3$ composite films. All perfectly annealed garnet layers and garnet-bismuth oxide composite films were characterized using different technologies to investigate their optical, magnetic and MO properties.

In garnet thin films synthesis, finding an optimized annealing regime is always one of the most important key factors for achieving successful material development outcomes. Fig.4.3 shows a photograph of (Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ having 37 vol. % of excess Bi$_2$O$_3$) composite films on Corning 1737 glass (larger sample) and on a GGG (smaller sample) substrate having hazy and optically damaged (scatterer-type) surfaces due to over-annealing. These films were annealed for only 30 minutes at 520°C, with a temperature ramp (up/down) rate of 5°C/min. However, this amount of thermal exposure was already excessive, due to the rather high bismuth content of the deposited layers. It is evident that either the annealing temperature or the annealing duration, or both, were not optimized to form optically-flat nano-crystalline layers from the amorphous phase of these garnet-oxide composites. Even though these films were optically spoiled, they still demonstrated some useful MO properties in terms of Faraday rotation per film thickness unit.
Fig. 4.3 Photographs of an optimally annealed garnet-oxide composite thin film and two over-annealed films of composition type Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ sputtered onto Corning 1737 (larger samples) and GGG (smaller sample) substrates. The transparent film (on the left) has a smaller thickness and high surface quality. The two over-annealed films were oven-treated at 520 °C for 30 min.

A series of annealing experiments have been performed with two different batches of garnet-Bi-oxide composite films of composition types Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17 vol. %) and Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. %) to observe the effects of annealing on the properties of these types of garnets and also to study the annealing behaviour and the crystallization kinetics of these garnet materials. The effects of isothermal annealing on the physical (both optical and MO) properties and on magnetic behavior of both types of garnet-oxide composite films are described in the next chapter of this thesis.

4.1.3 Thin film garnet materials characterization

Optimally annealed and high quality garnet and garnet-Bi-oxide composite films have been characterized by investigating the micro-structure, optical, magnetic and MO properties. The crystal structure and impurity phases of garnet and garnet-bismuth oxide thin films, of type (BiDy)$_3$(FeGa)$_5$O$_{12}$, were analysed using X-ray diffractometry (XRD) data generated by Panalytical Xpert Pro X-ray diffractometer configured for near-grazing-incidence powder diffraction measurements using the CuK$_{\alpha 1}$ ($\lambda = 0.15406$ nm) radiation. The optical properties of garnet films were investigated by measuring the transmission spectra using UV/Visible spectrophotometer and also by deriving the absorption coefficient spectra. The most important magnetic and MO properties of the garnet films were characterized by measuring the Faraday rotation angle and Faraday rotation hysteresis loops. The specific Faraday rotation measurements were performed almost across the entire visible spectral region by using several laser light sources, a
Thorlabs PAX polarimeter and an electromagnet. The magnetic domain patterns of garnet films were observed using a transmission-mode polarizing microscope (Leitz Orthoplan).

4.2 Bi-substituted Ga-doped dysprosium iron garnets

Highly-Bi-substituted Dy-doped-iron-garnet described by the generic formula (Bi,Dy)\textsubscript{3}(Fe,Ga)\textsubscript{5}O\textsubscript{12} and its nanocomposite (co-sputtered garnet-Bi-oxide composite layers) derivatives of type (Bi,Dy)\textsubscript{3}(Fe,Ga)\textsubscript{5}O\textsubscript{12}; Bi\textsubscript{2}O\textsubscript{3} have been sputtered and synthesized as high-quality thin films on optical substrates. The sputtering conditions and the process parameters used to deposit the garnet and garnet-oxide composite amorphous layers with highly uniform quality are explained in Table 4.1.

<table>
<thead>
<tr>
<th>Sputtering process parameters</th>
<th>Values &amp; comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target stoichiometry</td>
<td>Bi\textsubscript{2}Dy\textsubscript{1}Fe\textsubscript{5-x}Ga\textsubscript{x}O\textsubscript{12} (where x=1 and 0.7) and Bi\textsubscript{2}O\textsubscript{3} (materials’ purity 99.99%)</td>
</tr>
<tr>
<td>Sputter gas and pressure</td>
<td>Argon (Ar), P(total) = 1 mTorr</td>
</tr>
<tr>
<td>Base pressure (inside the chamber)</td>
<td>P(base)&lt;1-2 E-6 Torr</td>
</tr>
<tr>
<td>RF power densities for garnets</td>
<td>3.3 – 7 W/cm\textsuperscript{2} (150-320 W)</td>
</tr>
<tr>
<td>RF power densities for Bi\textsubscript{2}O\textsubscript{3}</td>
<td>0.44 – 0.88 W/cm\textsuperscript{2} (20-40 W)</td>
</tr>
<tr>
<td>Deposition rates for garnets</td>
<td>3.5-8.7 nm/min</td>
</tr>
<tr>
<td>Deposition rates for Bi\textsubscript{2}O\textsubscript{3}</td>
<td>1.2-5 nm/min</td>
</tr>
</tbody>
</table>

The composition optimization for the garnet-oxide composite derivatives was performed using variation of RF power density to the separate targets used to fabricate the garnet-Bi-oxide nano-composites. Individually measured deposition rate of each target by using a well calibrated quartz crystal sensor were counted to calculate the volumetric concentration of excess bismuth oxide content into the composite films reached during the deposition process. Using the partial deposition rates (nm/min) of both targets, the estimated amount of volumetric concentration of excess bismuth oxide for the composite layers were calculated by using the following formula as stated below.
Deposition rate of Bi$_2$O$_3$ Vol. % of Bi$_2$O$_3$ = \frac{\text{Deposition rate of Bi$_2$O$_3$}}{\text{Total deposition rate (garnet + Bi$_2$O$_3$)}}

Table 4.2 shows the summary of composition adjustment for Bi$_2$Dy$_{1}$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ composite films and table 4.3 for the composite films of composition type Bi$_2$Dy$_{1.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ prepared on both GGG and glass (Corning 1737) substrates.

Table 4.2 Summary of the composition adjustment used to fabricate several batches of Bi$_2$Dy$_{1}$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ garnet-oxide composite films on GGG and glass (Corning 1737) substrates.

<table>
<thead>
<tr>
<th>Composition type</th>
<th>Deposition rate of garnet (nm/min)</th>
<th>Deposition rate of Bi$_2$O$_3$ (nm/min)</th>
<th>Total (garnet+oxide) deposition rate (nm/min)</th>
<th>Vol. % of Bi$_2$O$_3$ in composite films</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 150 W Bi$_2$O$_3$</td>
<td>3.77</td>
<td>3.6</td>
<td>7.37</td>
<td>48.85</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 60 W Bi$_2$O$_3$</td>
<td>8.33</td>
<td>1.7</td>
<td>10.03</td>
<td>16.97</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 90 W Bi$_2$O$_3$</td>
<td>8.33</td>
<td>2.353</td>
<td>10.865</td>
<td>23.33</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 120 W Bi$_2$O$_3$</td>
<td>8.33</td>
<td>3.2</td>
<td>11.53</td>
<td>27.75</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 150 W Bi$_2$O$_3$</td>
<td>8.33</td>
<td>3.6</td>
<td>11.93</td>
<td>30.18</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$</em>{1}$Fe$_4$Ga$<em>1$O$</em>{12}$ + 180 W Bi$_2$O$_3$</td>
<td>8.33</td>
<td>4.11</td>
<td>12.44</td>
<td>33.04</td>
</tr>
</tbody>
</table>
Table 4.3 Summary of the composition adjustment used to fabricate several batches of Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ garnet-oxide composite films on GGG and glass (Corning 1737) substrates.

<table>
<thead>
<tr>
<th>Composition type</th>
<th>Deposition rate of garnet (nm/min)</th>
<th>Deposition rate of Bi$_2$O$_3$ (nm/min)</th>
<th>Total (garnet+oxide) deposition rate (nm/min)</th>
<th>Vol. % of Bi$_2$O$_3$ in composite films</th>
</tr>
</thead>
<tbody>
<tr>
<td>175 W Bi$<em>2$Dy$<em>1$Fe$</em>{4.3}$Ga$</em>{0.7}$O$_{12}$ + 25 W Bi$_2$O$_3$</td>
<td>4.47</td>
<td>1.65</td>
<td>6.12</td>
<td>26.96</td>
</tr>
<tr>
<td>200 W Bi$<em>2$Dy$<em>1$Fe$</em>{4.3}$Ga$</em>{0.7}$O$_{12}$ + 25 W Bi$_2$O$_3$</td>
<td>5.33</td>
<td>1.65</td>
<td>6.98</td>
<td>23.64</td>
</tr>
<tr>
<td>250 W Bi$<em>2$Dy$<em>1$Fe$</em>{4.3}$Ga$</em>{0.7}$O$_{12}$ + 25 W Bi$_2$O$_3$</td>
<td>7.03</td>
<td>1.65</td>
<td>7.65</td>
<td>19</td>
</tr>
<tr>
<td>300 W Bi$<em>2$Dy$<em>1$Fe$</em>{4.3}$Ga$</em>{0.7}$O$_{12}$ + 25 W Bi$_2$O$_3$</td>
<td>8.16</td>
<td>1.65</td>
<td>9.81</td>
<td>16.82</td>
</tr>
<tr>
<td>320 W Bi$<em>2$Dy$<em>1$Fe$</em>{4.3}$Ga$</em>{0.7}$O$_{12}$ + 20 W Bi$_2$O$_3$</td>
<td>8.96</td>
<td>1.2</td>
<td>10.16</td>
<td>11.81</td>
</tr>
</tbody>
</table>

Significantly improved optical transparency has been obtained in the co-sputtered garnet layers in the visible spectral range as compared to the typical garnet types deposited without co-sputtering Bi$_2$O$_3$, as shown in Fig. 4.4(a). The presence of excess bismuth oxide content was intended to form an amorphous bismuth oxide-dominated matrix into which the garnet grains would be embedded after the crystallization process. The base garnet compositions (Bi$_2$Dy)$_3$(Fe,Ga)$_5$O$_{12}$ provide the necessary level of uniaxial magnetic anisotropy in RF sputtered films, while the extra dopants (gallium and dysprosium) introduced into the base garnet composition diminish the saturation magnetization and reduce the Faraday rotation but increase the optical transmission as well as the magnetostriction coefficients of the thin films. Very small garnet grains of crystallite size 30-50 nm have been observed within an optimally annealed Bi$_2$Dy$_1$Fe$_2$Ga$_1$O$_{12}$ garnet thin film and the microstructure characterization result (TEM image shown in Fig. 4.4 (b)) obtained by using a transmission electron microscope confirmed the results obtained from XRD data [107].
4.2.1 Microstructure characterization

X-ray diffractometry (XRD) characterisation experiments have been performed with some of the as-deposited and annealed garnet and garnet-oxide composite films having different vol. % of excess Bi$_2$O$_3$ and the X-ray diffraction datasets obtained from the samples are shown in Fig. 4.5. All of the annealed garnet samples showed X-ray diffraction peaks at the sets of angles characteristic of cubic lattice structure and revealed the nanocrystalline microstructure of the annealed garnet materials and the body-centered cubic (bcc) lattice structure type with an identifiable impurity phase (Fe$_3$O$_4$) [108].

The intensities of iron-oxide diffraction peaks observed in the co-sputtered garnet films were found relatively much lower than those observed in the typical garnet films. The addition of extra Bi$_2$O$_3$ always reduced the intensities of the iron-oxide diffraction peaks which meant that there was less iron oxide present outside the garnet nanocrystallites. There were no bismuth oxide diffraction peaks characteristics observed in co-sputtered garnet samples. The lattice parameters and the lattice constant for highly-Bi-substituted gallium doped iron garnet have been calculated using identifiable diffraction lines in trace 4 of Fig. 4.5, obtained data are shown in Table. 4.2.
Fig. 4.5 X-ray diffraction datasets obtained from several types of garnet and garnet-oxide composite layers having different vol. % of extra Bi$_2$O$_3$ deposited onto glass substrates, including an amorphous (as-deposited) layer of Bi$_2$Dy$_4$Fe$_4$Ga$_1$O$_{12}$.

To calculate the lattice constant of the garnet thin films materials, the following formula (Eq. 4.1) has been used (with which a calculation of the unperturbed lattice constant $a_0$ of (BiDy)$_3$(FeGa)$_5$O$_{12}$ garnet materials was made) [109].

$$a_0 = 12.373 A + Bi(f.u.) \times 0.0828 + Dy(f.u.) \times 0.0097 - Ga(f.u.) \times 0.0151$$ (4.1)

where the numbers of Bi, Dy and Ga atoms per garnet formula unit (f.u.) are used. Using Eq. (4.1) and approximating the gallium content to be near 1.0 formula units, the expected composition of a garnet with an unperturbed lattice parameter of $a_0 = 12.563$ Å to be close to Bi$_{12.4}$Dy$_{0.6}$Fe$_4$Ga$_1$O$_{12}$ was derived which agreed with the EDX microanalysis results. EDX microanalysis was performed to determine the compositional element of the garnet and garnet-oxide composite films in order to compare the compositions of films of the same material type in the amorphous (as-deposited) and polycrystalline phases.
Table 4.4 XRD pattern indexing results and lattice constant calculation of a high-MO-performance garnet-Bi-oxide composite sample of type Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (23 vol. %) annealed for 2 hours at 580°C (trace 4 in Fig. 5).

<table>
<thead>
<tr>
<th>2Θ (degrees)</th>
<th>(hkl) plane</th>
<th>Lattice constant (Å)</th>
<th>Lattice constant (averaged, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.25</td>
<td>211</td>
<td>12.581</td>
<td></td>
</tr>
<tr>
<td>19.95</td>
<td>220</td>
<td>12.578</td>
<td></td>
</tr>
<tr>
<td>26.55</td>
<td>321</td>
<td>12.551</td>
<td></td>
</tr>
<tr>
<td>28.35</td>
<td>400</td>
<td>12.582</td>
<td></td>
</tr>
<tr>
<td>31.8</td>
<td>420</td>
<td>12.574</td>
<td></td>
</tr>
<tr>
<td>34.95</td>
<td>422</td>
<td>12.566</td>
<td>12.563</td>
</tr>
<tr>
<td>39.25</td>
<td>521</td>
<td>12.562</td>
<td></td>
</tr>
<tr>
<td>50.35</td>
<td>444</td>
<td>12.545</td>
<td></td>
</tr>
<tr>
<td>52.55</td>
<td>640</td>
<td>12.548</td>
<td></td>
</tr>
<tr>
<td>54.65</td>
<td>642</td>
<td>12.557</td>
<td></td>
</tr>
<tr>
<td>58.75</td>
<td>800</td>
<td>12.563</td>
<td></td>
</tr>
<tr>
<td>68.45</td>
<td>842</td>
<td>12.552</td>
<td></td>
</tr>
</tbody>
</table>

The calculated (averaged) lattice constants of crystallized Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ and that of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (22 ±3 vol. %) grown on both GGG (111) substrate were 12.520 Å and 12.579 Å [108].

The crystallite sizes of garnet materials have been estimated using the diffraction peaks’ linewidth broadening data and the Scherrer’s equation

$$D = \frac{K \lambda}{B \cos(\Theta_B)}$$

(4.2)

where $D$ is the crystallite particle size (nm), $\lambda$ is the X-ray wavelength, $\Theta_B$ is the Bragg diffraction angle (radians), and $B$ is the full-width at half-maximum (FWHM, in radians) of the diffraction peak at $\Theta_B$. The coefficient $K$ in (4.2) is a constant and is taken to be equal to 0.9 [110]. Using (420) diffraction peaks of garnet (Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$) films deposited onto a glass (Fig. 4.5, trace 2) at $\Theta_B = 15.979^\circ$ (FWHM of these peaks was measured to be about 0.22°), a crystallite size of about 37 nm was deduced for Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ using Scherrer’s equation. The average crystallite size for all the garnet-oxide composite materials tested was found to be in the same order. Two diffraction peaks (at 2Θ angles near 44.5 and 65 degrees) were found
to be present (with some intensity variations) in all material samples measured, including the as-deposited as well as annealed layers on all substrate types.

### 4.2.2 Optical properties

The transmission spectra measurements for the Bi$_2$Dy$_4$Fe$_4$Ga$_1$O$_{12}$, Bi$_2$Dy$_4$Fe$_4$$_{0.3}$Ga$_{0.7}$O$_{12}$ and also for all the garnet-bismuth oxide composite films (as deposited and annealed) were performed by using Beckman Coulter DU 640B UV-visible spectrophotometer. The measured transmission spectra of all the garnet and garnet oxide composite films were very close to the modelled transmission spectra (within the spectral window between 500-1100 nm) of our films. It was confirmed that the garnet and garnet-oxide composites had the refractive index spectra which are very close to the reliably-known index spectra of Bi$_2$Dy$_4$Fe$_4$Ga$_1$O$_{12}$ (measured by using spectroscopic ellipsometry) in its amorphous and crystallized phases [19]. The fitting of the measured transmission spectra of the garnet films with the modelled transmission spectra allows re-confirming the physical layer thicknesses of the sputtered films. The film thicknesses were derived to within an estimated of ± 5% accuracy using a custom-developed software. Also the absorption spectra of garnet and garnet-oxide composite films were derived by using the iterative fitting of the spectral features observed in the measured and modelled transmission spectra of the films. The absorption spectra of the best performing high-quality garnet and garnet-oxide composite films (as-deposited and optimally annealed to form high-quality nano-crystalline phase) are shown in Fig. 4.6. It was observed that the addition of Bi$_2$O$_3$ content from a separate target during the deposition of thin films reduces the optical absorption across most of the visible and near-IR spectral regions and the quality of the co-sputtered garnet films in terms of optical transparency was completely dependent on the volumetric concentration of excess Bi$_2$O$_3$. The influence of excess bismuth oxide was observed in terms of optical loss inspection (optical absorption) and it was found that the extra bismuth oxide reduced the optical absorption, the summary of optical absorption achieved in garnet and garnet-oxide composite films having different vol. % of excess Bi$_2$O$_3$ is shown in Fig. 4.7. Also the effects of substrates on optical absorption were observed very carefully and similar trends in the absorption spectra behaviour were found in the composite garnet-oxide materials deposited onto glass substrates. The lowest absorption coefficients achieved in the composite garnet-oxide films were in between 1100-1200 cm$^{-1}$ at 635 nm which is comparable with that of epitaxial mono-crystalline films [23].
Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ garnet film (1000nm) on GGG, amorphous
Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 23.3% vol) composite on GGG, amorphous
Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ garnet film on GGG, annealed for 1 hr @ 700 C
Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 23.3% vol) composite on GGG, annealed for 2 hrs @ 580 C

Fig. 4.6 Derived absorption coefficients spectra of sputtered Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ and Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ garnet layers and these of the garnet-oxide composites (best-performing types) sputtered onto GGG (111) substrates (measured in amorphous-phase and optimally-annealed nanocrystalline films).

Amorphous Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ on GGG, typical 1000 nm samples (1)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 17 vol.%), 1110 nm sample (2)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 23.3 vol.%), 1090 nm sample (3)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 27.7 vol.%), 620 nm sample (4)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 30 vol.%), 600 nm sample (5)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 33 vol.%), 565 nm sample (6)
Composite layer of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (est. 49 vol.%), 535 nm sample (7)

Fig. 4.7 Derived absorption coefficients spectra of sputtered Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ and Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ composite layers on GGG (111); amorphous layers deposited at 250 °C substrates’ temperature.
4.2.3 Magnetic and magneto-optical properties

The Faraday rotation per unit film thickness for the garnet and garnet-oxide composite films has been measured using the visible spectral range plane-polarized light source. Fig. 4.8 shows the measured specific Faraday rotation spectrum of the garnet films of type Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ and measured specific Faraday rotation data points of the garnet films of composition Bi$_2$Dy$_{1.3}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$ and also some of the best performing garnet-oxide nano-composite films having different vol. % of Bi$_2$O$_3$. Stronger Faraday rotation performance with near-100% remnant magnetization has been observed in all the garnet-oxide composite films being optimally annealed compared to the typical garnet materials. At the same time a range of garnet-oxide composite films possessed lower optical absorption in the visible spectral range which leads to improve the MO quality (figure of merit) of the garnet-oxide nano-crystalline thin films materials. The highest values of specific Faraday rotation obtained in garnet-oxide composite films were more than 10°/µm at 532 nm, 2.6°/µm at 635 nm, and 1.9°/µm at 670 nm and all the garnet films possessed their useful magnetic memory properties (near-square hysteresis loops). All the garnet-oxide composite films possessed significantly high MO figure of merit, which is defined by the doubled ratio of the specific Faraday rotation to the material absorption (2$\Theta_F/\alpha$). The best MO figure of merit of the composite films measured so far at 635 nm was 43°(±2°), which makes these materials very attractive for nano-structured magneto-photonic components and devices.
The specific Faraday rotation and MO figure of merit spectra have been observed and studied as a function of the estimated volumetric fraction (approximated quantification of the excess Bi$_2$O$_3$ fractions by volume, calculated using the partial and total deposition rates) of bismuth oxide and the summary of measured Faraday rotation as well as the MO figure of merit in garnet and garnet-oxide composite films is presented in Fig. 4.9. It was found that the specific Faraday rotation at 532 nm measured in composite films type Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ increases with the increase of excess Bi$_2$O$_3$ content up to about 25 vol. %, while at 635 nm, the best specific Faraday rotation peaks at the range of excess oxide fractions of between 16-20 volume percent. There was a drop in specific Faraday rotation at 635 nm observed after reaching about 25 vol. % excess Bi2O3 content in the film (Fig 4.9(a)). This is partly due to some impurity phase formation, but is also mainly due to the increase in the volume of material in the amorphous matrix surrounding the garnet grains. This significant drop in Faraday rotation at 635 nm did not affect the MO quality of the materials as the MO quality factor is a function of Faraday rotation and the optical absorption.
Fig. 4.9 Summary of Specific Faraday rotation (measured at remanent magnetization states) of the co-sputtered annealed Bi$_2$Dy$_1$Fe$_4$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (a) and Bi$_2$Dy$_1$Fe$_4$Ga$_{1}$O$_{12}$: Bi$_2$O$_3$ (b) composite garnet films deposited onto GGG (111) substrates at 532 nm (dotted lines) and 635 nm (solid lines) as a function of the estimated excess volumetric content of Bi$_2$O$_3$, and the indicated values are MO figures of merit measured using 532 nm and 635 nm laser sources. Here zero percent of excess bismuth oxide containing garnet films means the typical garnet thin film materials of the corresponding stoichiometry type not mixed with any extra oxide content.

On the other hand, in the garnet-oxide nanocomposite films of composition type Bi$_2$Dy$_1$Fe$_4$Ga$_{1}$O$_{12}$: Bi$_2$O$_3$ having the excess bismuth oxide content greater than about 25
vol. %, some surface degradation often occurred after the annealing processes, which led to the significant scattering losses, and consequently, the reduction in the MO figure of merit (Fig. 4.9(b)). Nevertheless, films with up to 50 vol. % of excess $\text{Bi}_2\text{O}_3$ were synthesized and annealed rather successfully, and these showed about 55-60% of the specific Faraday rotation measured in the undiluted-garnet films as well as high MO figure of merit. These highly-diluted composite films might have very small and isolated garnet grains embedded into the surrounding amorphous matrix filled predominantly with bismuth oxide, which remarkably improved optical transparency of these films in the visible spectral range.

Fig. 4.10 shows the measured hysteresis loops of garnet and garnet-oxide composite films having different volumetric fraction of extra $\text{Bi}_2\text{O}_3$. Nearly square hysteresis loop of Faraday rotation has been obtained in a 1 µm thick $\text{Bi}_2\text{Dy}_1\text{Fe}_4\text{Ga}_1\text{O}_{12}$ garnet layer with excellent magnetic memory properties; the coercive force was about 200 Oe (Fig. 4.10(a)). It is found that the values of coercive force for this type of material were also dependent on the films’ thickness, and coercive force values of about 1000 Oe were measured in a 4 µm-thick film of the same composition and reported in Ref [19]. The hysteresis loops of all garnet-oxide composite films tested were found to be practically square-shaped. The variation and difference of coercive force and switching field values have been observed with the variation of additional extra bismuth oxide content into the garnet composite films revealing that it is possible to engineer the magnetic characteristics of the co-sputtered thin films garnet materials suitable for different ultra-fast switching applications.
Fig. 4.10 Measured hysteresis loop of Faraday rotation in (a) Bi$_2$Dy$_1$Fe$_3$Ga$_3$O$_{12}$ garnet layer; (b) Bi$_2$Dy$_1$Fe$_4$Ga$_3$O$_{12}$: Bi$_2$O$_3$ garnet-oxide composite films of slightly varying the extra bismuth oxide content into the garnet, the hysteresis loop of Faraday rotation was measured at 532 nm.

The photographs of magnetic domain patterns observed in two different garnet-oxide composite films using a transmission-mode Leitz Orthoplan polarizing microscope are shown in Fig. 4.11. The domain structures’ observation have been performed with the optimally annealed (after conducting the heating and cooling processes) thin films in a demagnetized state. The high-contrast domain structures obtained in garnet-oxide composite films Bi$_2$Dy$_1$Fe$_3$Ga$_3$O$_{12}$:Bi$_2$O$_3$ (est. 23 vol. %) of 1000 nm thicknesses and 850 nm thick Bi$_2$Dy$_1$Fe$_4$Ga$_3$O$_{12}$:Bi$_2$O$_3$ (est. 24 vol. %) sputtered onto GGG (111) substrates confirms the presence of strong uniaxial magnetic anisotropy with the direction of the easy magnetization axis perpendicular to the film’s plane.
Fig. 4.11 Magnetic domain patterns observed using a transmission-mode polarizing microscope in two different demagnetized garnet-oxide composite films having different vol. % of extra bismuth oxide sputtered onto GGG (111) substrates (a) Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$:Bi$_2$O$_3$ (est. 23 vol. %); (b) Bi$_2$Dy$_1$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$:Bi$_2$O$_3$ (est. 24 vol. %) and 1 µm thick Bi$_2$Dy$_1$Fe$_5$Ga$_5$O$_{12}$ garnet film on GGG.

The garnet-oxide composite films fabricated by adding the excess Bi$_2$O$_3$ content into the garnet structure of type (BiDy)$_3$(FeGa)$_5$O$_{12}$ have exhibited excellent optical and magneto-optical properties as well as uniaxial magnetic anisotropy simultaneously. These materials are highly attractive for visible and near-infrared range magneto-optics.

4.3 Bi-substituted Al-doped lutetium iron garnets

Bi-substituted Al-doped lutetium iron garnets defined by the generic formula (Bi,Lu)$_3$(Fe,Al)$_5$O$_{12}$ and its nanocomposite co-sputtered derivatives (Bi,Lu)$_3$(Fe,Al)$_5$O$_{12}$: Bi$_2$O$_3$ featuring the magneto-soft behavior have been another research of interest. This type of material also possessed similar optical properties and crystallization behavior as obtained with the first type of materials but it possessed very different magnetic and magneto-optical properties. The motivation for the synthesis of (Bi,Lu)$_3$(Fe,Al)$_5$O$_{12}$ films on optical substrates (glass and GGG) was to establish the technology for the manufacture of magneto-soft garnet layers with high Bi substitution (approaching 2.0 formula units and above), magnetization vector direction close to being in the film’s plane, and possessing a high MO figure of merit in the visible and near-infrared ranges. The synthesis of highly Bi-substituted iron garnet films of the composition type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ using any physical vapor deposition process was never reported in technical literature before, and we achieved the manufacture of new high-quality garnet thin film material featuring a strong in-plane magnetization component [111]. The lattice parameter of this new engineered material was kept close to that of gadolinium gallium garnet (12.383 Å), since the lattice parameter of this new garnet material was initially calculated based on the methods described in Ref [109]. High-crystalline-quality iron-garnet materials with high Bi
substitutions typically possess crystal lattice parameters exceeding that of GGG significantly and have been deposited so far mostly onto specialized and somewhat rare large-parameter substrate types, like GSGG. In addition, it is rather difficult to obtain garnet-phase layers with Bi substitutions being as large as 1.8 f.u. using LPE processes; however RF sputtering of such materials from oxide-mix-based targets has been demonstrated successfully [23]. This has opened the way for the development of closely substrate-matched and highly-Bi-substituted garnet layers exhibiting very strong specific Faraday rotation and strong in-plane magnetization component (weak uniaxial magnetic anisotropy) simultaneously.

The sputtering target of stoichiometry $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ has been selected as deposition material source and to deposit several batches of garnet and also garnet-$\text{Bi}_2\text{O}_3$ composite layers using essentially the same deposition techniques as for Bi-substituted dysprosium iron garnet. Highly Bi-substituted lutetium iron-aluminium garnet and also garnet-$\text{Bi}_2\text{O}_3$ nanocomposite layers having different volumetric fractions of extra $\text{Bi}_2\text{O}_3$ (4.5-20 vol. %) of different thicknesses have been fabricated onto optical substrates using physical vapour deposition (RF magnetron sputtering) technique. The details of sputtering process parameters and conditions are summarized in Table. 4.3. All the as-deposited (amorphous) garnet and garnet-oxide thin films were subjected to crystallize using optimized annealing heat treatment processes. The film thicknesses were monitored during the deposition processes using in-situ laser reflectometry and were also re-measured after the deposition using their transmission spectra obtained with a UV/visible spectrophotometer and our thickness-fitting software [18, 112].
Table 4.5 Sputtering parameters and process conditions used for the deposition of magneto-optic Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet layers and garnet-bismuth oxide nanocomposite derivatives.

<table>
<thead>
<tr>
<th>Sputtering process parameters</th>
<th>Values &amp; comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering targets composition</td>
<td>Bi$<em>{1.8}$Lu$</em>{1.2}$Fe$<em>{3.6}$Al$</em>{1.4}$O$_{12}$ (materials’ purity 99.99%) and Bi$_2$O$_3$ (99.999%)</td>
</tr>
<tr>
<td>Target size</td>
<td>3´´ (diameter) with the material layer thickness of 1/8´´</td>
</tr>
<tr>
<td>Background Pressure</td>
<td>P(base) &lt; 1-2·10$^{-6}$ Torr</td>
</tr>
<tr>
<td>Process gas and pressure</td>
<td>Argon, P(Ar) = 1mTorr</td>
</tr>
<tr>
<td>RF power density at targets</td>
<td>Typically 3.7 W/cm$^2$ (170 W) for garnet and 0.22-0.55 W/cm$^2$ (10-25 W) for Bi$_2$O$_3$</td>
</tr>
<tr>
<td>Substrate-target distance</td>
<td>18-20 cm</td>
</tr>
<tr>
<td>Substrate temperature during deposition</td>
<td>250-680 °C for typical garnet, and 250 °C for garnet-oxide composite layers</td>
</tr>
<tr>
<td>Substrate types</td>
<td>Glass (Corning Eagle XG) and monocrystalline GGG (111)</td>
</tr>
<tr>
<td>Deposition rates</td>
<td>4-6 nm/min for garnet; 0.7-1.3 nm/min for Bi$_2$O$_3$</td>
</tr>
</tbody>
</table>

The synthesis of co-deposited nanocomposites of type (Bi,Lu)$_3$(Fe,Al)$_5$O$_{12}$: Bi$_2$O$_3$ has led to films with improved optical transparency and therefore with better MO quality as was expected. The optical, magnetic and magneto-optical properties of this type of MO film and the effect of excess Bi$_2$O$_3$ concentration on the magnetic properties of these materials have been investigated and found very attractive and promising properties suitable for different applications such as sensing and imaging.

### 4.3.1 Optical properties

The optimally annealed high-quality garnet and garnet-oxide composite thin films demonstrated an attractive combination of rather high specific Faraday rotation (confirming high Bi substitution levels achieved) and low optical absorption across large parts of the visible spectral range. Very good transparency was observed across the near-infrared range. Fig. 4.12 shows the typical absorption spectrum of crystallized Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ layers deposited onto GGG (111) substrates, with the upper and lower limits for the absorption coefficients.
Fig. 4.12 Derived absorption coefficient spectrum showing the upper (red colour) and lower limits (brown colour) of $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ garnet films prepared onto a GGG (111) substrate; The data points for the MO figure of merit measured at 532, 635 and 660 nm with their associated error bars are shown in the inset.

Fig. 4.13 Derived absorption spectra of $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ and several $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$: $\text{Bi}_2\text{O}_3$ composite films sputtered onto GGG (111) substrates; the excess content of $\text{Bi}_2\text{O}_3$ and the annealing regimes used for the typical garnet and the co-sputtered composite films are mentioned.

Similar spectra of absorption coefficients were observed on the samples sputtered onto glass (Corning Eagle XG) substrates also. Significantly lower absorption coefficients
were obtained in garnet-oxide composite films across the visible spectral region compared to $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ garnet layers as shown in Fig. 4.13. The additional bismuth oxide helps improve the optical transparency by surrounding MO garnet phase grains with non-magnetic transparent bismuth oxide.

4.3.2 Magnetic and magneto-optical properties

Faraday rotation measurements have been performed with a well calibrated measurement setup of Thorlabs PAX polarimeter (high dynamic range of 70 dB, a broad wavelength range, and an accuracy of ±0.2°) and custom-made electromagnet. The maximum (measured in optimally-annealed films on GGG substrates) values of Faraday rotation per film thickness of this garnet material type were around 5.9 deg/µm at 532 nm, 1.6 deg/µm at 635 nm and 1.07 deg/µm at 660 nm, and the films also had relatively low absorption coefficient, which led to high MO figure of merit. The best measured MO quality factors ($2\Theta_F/\alpha$) of $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ garnet layers deposited onto GGG (111) substrates and obtained values of 13.9° (±1.6°) at 532 nm, 15.7° (±2°) at 635 nm and 12.7° (±0.7°) at 660 nm; these values were lower by about 15-20% in films deposited onto glass. The addition of extra bismuth oxide didn’t have much impact on the Faraday rotation of the composite films but it did improve the optical quality noticeably, consequently improving the magneto-optic quality in terms of MO figure of merit up to more than 50° at 635 nm. The best-achieved (to date) MO performance characteristics of our garnet and garnet-oxide composite films for two important wavelengths in the visible spectral region are shown in Fig. 4.14.
Fig. 4.14 Measured MO quality factor in terms of figure of merit of typical Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet layer deposited at 250 °C and 680 °C substrate temperature and several best annealed composite Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ films having 4.5 vol. % excess Bi$_2$O$_3$ onto GGG (111) substrate.

Fig. 4.15 shows the hysteresis loops of specific Faraday rotation measured at 532 nm in films sputtered onto GGG (111) and also glass substrates using 250°C substrate temperature (a, b) and also the same data for a film deposited onto GGG at 680°C (c). The measured coercive force for the typical garnet films of composition type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ sputtered at 250°C on GGG substrates was about 45 Oe, while the coercivity of the films on glass substrates was near 100 Oe (Fig 4.15 (a, b)).
Fig. 4.15 Measured Hysteresis loops of specific Faraday rotation at 532 nm in sputtered Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet films deposited at 250 °C onto (a) GGG substrate (annealed for 1 h at 650 °C), (b) glass substrate (annealed for 3 h at 630 °C). Insets show the measured coercive force, saturation field and the magnetic field sensitivity values at 532 and 635 nm within the linear ranges of magnetization, and (c) hysteresis loop of specific Faraday rotation measured at 532 nm in sputtered Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet films of 650 nm deposited onto GGG at 680 °C substrate temperature annealed for 3 h at 630 °C.
Much lower coercive force value of below 20 Oe has been obtained in films of composition type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ prepared onto GGG substrates at a higher substrate temperature of 680°C garnet films of 650 nm thickness, annealed for 3 h at 630°C. The effects of adding bismuth oxide on the coercivity of the films sputtered onto both GGG and glass substrates have been observed and lower coercive force values have been obtained in composite films compared to the typical garnet films sputtered onto both types of substrates (Fig. 4.16).

During hysteresis measurements, the external magnetic field was applied in the direction perpendicular to the film plane, and parallel to the light propagation direction. The almost-linear character of magnetization curves observed below saturation indicates that a significant component of the film’s magnetization lies in the film plane. However, the magnetization vectors of the films on both substrate types also had a perpendicular component, which resulted in the observations of maze-type magnetic domain patterns by polarization microscopy and also using magnetic force microscopy. Within the linear magnetization range, a rather high Faraday-effect magnetic field sensitivity (the ratio of increments of Faraday rotation to magnetic field) of up to 42.8 °/(cm·Oe) was measured at 635 nm, which even exceeds the previously-reported value of 13 °/(cm·Oe) measured in epitaxial (BiLu)$_3$(FeGa)$_5$O$_{12}$ films obtained by LPE [113].
Typical Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet film on GGG; $H_c = (45 \pm 5)$ Oe

Composite Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol.%) film on GGG; $H_c = (30 \pm 5)$ Oe

Typical Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet film on glass; $H_c = (100 \pm 5)$ Oe

Composite Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (12.5 vol.%) film on glass; $H_c = (80 \pm 5)$ Oe

Fig. 4.16 Measured Hysteresis loops of Faraday rotation at 532 nm in (a) typical sputtered Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ layer on GGG (annealed for 1 h at 650 °C) and Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. %) composite garnet films deposited onto GGG substrate (annealed for 3 h at 620 °C), (b) sputtered Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet films on glass substrate (annealed for 3 h at 630 °C) and Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (12.5 vol. %) composite garnet films deposited onto Glass substrate (annealed at 560 °C for 5 h).
The domain structures obtained in (BiLu)$_3$(FeAl)$_5$O$_{12}$ garnet type and its derivative garnet-oxide composite thin films have been observed in the absence of externally applied magnetic fields (Fig. 4.17). The domain widths of about 1 micron were observed in films of 1 µm thickness in the transmission mode. It is possible to achieve better crystalline quality, lower coercive force values and even higher magnetic field sensitivity in the films of this composition type sputtered onto GGG substrates, if high-substrate-temperature deposition regime is optimized to achieve the conditions suitable for epitaxial-quality layer growth (sputter epitaxy).

![Fig. 4.17 Regular maze-type magnetic domain patterns observed in sputtered and later oven-crystallized Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet films on GGG substrates deposited at (a) 250 °C T(sub) (annealed for 1 hr @ 650 °C); (b) 680 °C T(sub) (annealed for 3 hrs @ 630 °C); (c) Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. %) composite garnet films (deposited at 250 °C and annealed for 10 hrs @ 610 °C).](image)

The surface morphology as well as surface magnetic field distribution topography of Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ composite films having 4.5 vol. % and 12.5 vol. % of excess bismuth oxide sputtered onto GGG substrates have been characterized using atomic force microscopy (AFM) and magnetic force microscopy (MFM). Fig. 4.18 shows the scanning probe microscopy inspection results for garnet samples of composition Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. %) presented as 3D images of the surface features and surface magnetic field distribution (Fig. 4.18 (a and b)), and also shows the results for a Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (12.5 vol. %) film presented as 2D images (Fig. 4.18(c, d)). The garnet samples have been scanned using semi-contact mode of probe-interaction to obtain the feedback-phase and also the surface topography data simultaneously from the same scan area. The MFM cantilever tip used was cobalt-coated to enable the magnetic-force interaction representation through the phase of the cantilever feedback signal. Nano-crystalline surface microstructure and its associated surface roughness features of the garnet films have been observed from the obtained high-contrast images extracted from the measured feedback-phase images and
topography data. The magnetic domains structure and the map of magnetic interaction force between the cantilever tip and sample surface have also been imaged. The black-white color palette of image (Fig. 4.18(d)) represents the measured RMS strength of the AC magnetic interaction force between the tip and surface, and the color map shown was obtained using a halved algebraic sum of the phase image data map obtained and its inverted phase image data map, so that only the magnitude of the magnetic interaction force is represented. The white-colored pixels correspond to the minima locations of the magnetic interaction force.

![Fig. 4.18 Scanning-probe (AFM/MFM) images of garnet-oxide composite thin films having 4.5 vol. % and 12.5 vol. % extra bismuth oxide sputtered onto GGG (111) substrates. (a-b) 3D images showing the topography (5 × 5 µm sample area) of a 1050 nm thick Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$:Bi$_2$O$_3$ (4.5 vol.%), composite film annealed for 5 h at 615°C and its surface magnetism features measured across a 25 × 25 µm sample area; (c-d) 2D AFM topography (c) and (d) an AC magnetic force magnitude map (processed feedback phase image) obtained from a 1.2 × 1.2 µm sample area of a Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$:Bi$_2$O$_3$ (12.5 vol.%) nanocomposite film annealed for 5 h at 580°C.](image1)

It is important to note that Fig. 4.18 (a, b) revealed the addition of extra bismuth oxide results in bismuth-rich MO garnet-phase grains surrounded by transparent non-magnetic
bismuth oxide regions. While the measured overall Faraday rotation of the composite film was not improved, the measured overall optical transmission was considerably increased, leading to significant increase in MO figure of merit.

4.3.3 Microstructural properties

EDX microanalysis experiments have also been performed to determine the elemental composition of the thin garnet and garnet-oxide composite films and to compare the compositions of films of the same material type in the amorphous (as-deposited) phases. EDX measurements confirmed the presence of all elements expected to be present within films (measured element concentrations in atomic %) and the obtained output data is shown in Fig. 4.19. These elements can also belong to either the garnet crystallites in annealed films which can be confirmed by XRD measurements. The amount of bismuth (Bi) content in the composite layer is slightly larger than that of the typical garnet layer (atomic %) which is an indicative for the confirmation of getting extra bismuth into the dodecahedral site during the deposition process towards sputter a garnet layer having high bismuth content [108]. Based on these measurement data, the averaged composition of thin film was derived to be Bi$_{1.68}$Lu$_{0.656}$Fe$_{4.294}$Al$_{1.184}$O$_{12}$ which might be expected considering the sputtering target’s nominal stoichiometry and possible Bi content loss occurring during layer growth.
Fig. 4.19 EDX composition analysis results for (a) typical garnet films of composition $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ and (b) co-sputtered composite having excess bismuth oxide of 4.5 vol. % sputtered onto silicon (Si) substrates using the targets of nominal stoichiometry $\text{Bi}_{1.8}\text{Lu}_{1.2}\text{Fe}_{3.6}\text{Al}_{1.4}\text{O}_{12}$ and $\text{Bi}_2\text{O}_3$ onto Si substrate.

The ratio between the Fe and Al content in terms of atom number per formula unit is found slightly different from the estimated with large oxygen content (> 60 at. %) measured in all films. The presence of higher number of oxygen atoms in the thin garnet films is probably the cause of experimental errors; extra oxygen can be present either within the substrates or trapped within the film pores.
The excellent combinations of properties, together with the magnetically-soft behaviour, make these sputtered films of composition Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ very attractive for use in different magneto-optic applications and in novel photonic components, for example in garnet waveguides [114].

### 4.4 Magnetostatically-altered multilayer garnet thin film structures for engineering the magnetic properties

Multilayer garnet thin film structures are very attractive and useful for information technology as well as all-optical reconfigurable signal processing devices. However, in the device applications they are still very limited as it is difficult to fabricate high-quality thin film nano-structures (of either single- or multi-layer type) with a good degree of control over their magnetic behaviour, especially if the magnetic switching behaviour and magnetic anisotropy properties need to be adjustable. To realise special magnetic behaviours, which are not attainable using single-layer thin films of a chosen garnet material type, couple of batches of all-garnet multilayer structures were prepare using the above discussed record-performance highly-Bi-substituted iron garnet materials having very different magnetic behaviours (magnetic anisotropy, switching fields and saturation magnetizations). All garnet multilayer structures were prepared by sandwiching a garnet layer of composition type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ in between two layers of Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$ of same thickness (as shown in Fig. 4.20) to study and engineering of magnetic properties in multilayer thin film structures, and especially the ways of adjusting the coercive force and magnetic anisotropy properties. The multilayer structures were deposited onto gadolinium gallium garnet (GGG) and also onto glass (Corning Eagle XG) substrates. The structures were prepared on both substrate types in a single deposition run by sequential sputtering of layers using low-pressure argon plasma and a relatively low substrate temperature of 250°C. The all-garnet structures were as following (a) [Substrate/(500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)/(500 nm Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$]/(500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)], (b) [Substrate/(50 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)/(50 nm Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$]/(50 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)] and (c) [Substrate/(100 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)/(200 nm Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$]/(100 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)].
RF sputtering technique was used to deposit all-garnet multilayer structures as it allows precise control over the thin films deposition process parameters, and thus reducing the problem of synthesizing high-quality thin films and multilayer structures wherein each layer’s chemical composition (stoichiometry) must be controlled accurately. After the deposition the garnet multilayer structures have been subjected to high temperature oven-annealing process using optimized annealing regimes for simultaneously crystallizing both material types within these garnet multilayer structures. It was also difficult and needed a significant amount of experimental work to find optimum annealing regimes for the multilayer thin film structures. I was lucky enough and managed to find the optimum annealing regimes suitable to crystallize the multilayer structures containing two different garnets. Only the structure (a) has been characterized completely using the available characterization facilities at ECU, and it has been found that the structure possessed significantly improved magnetic properties [115]. The characterization process for the remaining two multilayer structures (b and c) to investigate their properties are under way; the results obtained will be compared with these obtained with the first structure and will be published elsewhere.
4.4.1 Optical properties

The physical thicknesses of each layer of the multilayer thin film were measured during the deposition processes using the in-situ laser reflectometer system and after the deposition the layer thicknesses of the structure were re-measured by applying the techniques that we used to characterize our garnet thin films (single layer). Fig. 4.21 shows the transmission spectra of all-garnet multilayer structure (a) obtained from an amorphous and a post-annealed sample, compared to the modelled transmission spectra of the same structure. The measured transmission spectra were very similar to the modelled transmission spectrum having a slight variation in transparency which was due to small variations in the refractive index and (especially) the variations in absorption spectra of both garnet types with the thermal treatment regime.

Fig. 4.21 Transmission spectra of [GGG / (500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$) / (500 nm Bi$_{1.8}$Lu$_{1.2}$Fe$_3.6$Al$_{1.4}$O$_{12}$) / (500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)] multilayer garnet structure, (green dotted line) is modelled transmission spectrum of this structure, (red line) is the measured transmission spectrum of a structure which was annealed with an optimized annealing regime (3h at 630 °C) and (blue dotted line) is the measured transmission spectrum of this structure obtained immediately after the deposition.

A non-polarizing beam-splitter cube (the reflectance of the cube at glass-air interfaces was about 4%) was used in the UV/Visible spectrophotometer for the reflectivity
measurements. The beam-splitter re-directs a part of the light source beam to be reflected off samples, with a silver mirror (200 nm silver layer deposited onto a glass substrate possessing approximately spectrally-flat 97% reflectance) being used as a reference mirror which also deflected the light toward the sample placed next to a cube side opposite to the side next to which the mirror was placed. The wavelength dependency of the cube’s internal diagonal reflectance was also measured and used to calculate the sample’s own reflectance at each wavelength from the spectrophotometer data obtained in (the only available) transmission measurement mode with and without the sample placed next to the cube’s side surface. The sample was placed with the garnet layer surface firmly against the glass cube side during the measurement. The absorption spectrum of the structure was derived from the measurements of the transmission and reflection spectra, using a very simple formula

\[ A \, (\%) = 1 - T - R \]  
\[ (4.3) \]

where \( A \) is the absorbed power fraction, \( T \) is the power transmission coefficient, and \( R \) is power reflectivity. A strong agreement was observed between the derived and modelled absorption spectra of the annealed multilayer garnet structure, as is shown in Fig. 4.22.

![Absorption spectra of [GGG / (500 nm Bi\textsubscript{2}Dy\textsubscript{1}Fe\textsubscript{4}Ga\textsubscript{1}O\textsubscript{12}) / (500 nm Bi\textsubscript{1.8}Lu\textsubscript{1.2}Fe\textsubscript{3.6}Al\textsubscript{1.4}O\textsubscript{12}) / (500 nm Bi\textsubscript{2}Dy\textsubscript{1}Fe\textsubscript{4}Ga\textsubscript{1}O\textsubscript{12})] multilayer garnet structure, (green dotted line) is modelled absorption spectrum of this structure, (red line) is the measured absorption spectrum of a structure which was annealed using an optimized annealing regime (3h at 630 °C).](image)
4.4.2 Magnetic properties

The measurements of Faraday rotation (total polarization plane azimuth rotation angle) for the all-garnet multilayer structure as well as the hysteresis loop of Faraday rotation have been performed using a 532 nm plane-polarized solid-state laser. A notably low coercive force and also rather significant uniaxial magnetic anisotropy (evidenced by the large remnant magnetization) was observed in the structure. The best (among all samples from the first deposition batch, which had different thermal treatment histories) Faraday rotation at 532 nm was measured in the multilayer structure was more than ± 3° (total angle), and the measured coercive force was about 100 Oe, with a value of saturation field of near 200 Oe.

![Fig. 4.23 Measured magnetic hysteresis loop in [Sub (GGG) / (500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$) / (500 nm Bi$_{1.8}$Lu$_{1.2}$Fe$_3.6$Al$_{1.4}$O$_{12}$) / (500 nm Bi$_2$Dy$_1$Fe$_4$Ga$_1$O$_{12}$)] multilayer all-garnet structure deposited onto GGG (111) substrate (and annealed for 3h at 630 °C after the deposition).](image)

Within the garnet thin-film multilayer structures, the effects of magnetostatic coupling between the different garnet layers of two different magnetic behaviour types controlled the overall magnetic properties of the structure. The intermediate layer of garnet having almost in-plane magnetization might have reduced the overall coercivity compared to that of the top and bottom magneto-hard garnet layers, whilst the strong perpendicular
magnetization of these two outer layers helped retain the magnetic memory properties in the behaviour of the multilayer structure.

### 4.4.3 Microstructural characterization

The microstructure observation (performed by using focused ion beam (FIB) milling cross-section) confirmed the successful crystallization of the entire multilayer structure without any significant incompatibilities (confirmed by the smooth interfaces between the layers as shown in Fig. 4.24) between the dissimilar high-bismuth-content MO garnet materials. Both types of magnetic materials into the structure were perfectly annealed after a single optimised (both the annealing temperature and time) thermal annealing process.

![FIB cross-sectional image](image)

**Fig. 4.24** FIB cross-sectional image (imaged by electron beam) of a 3-layer all-garnet structure which was subjected to annealing for 10 h at 630 °C. The thicknesses of all layers are almost the same and are close to 500 nm each, even though some measurement bars in the figure are inaccurate and show a smaller thickness.

The magnetic domain patterns were obtained in a perfectly annealed all-garnet multilayer structure is shown in Fig. 4.25. This image was taken after the structure was brought into a brief mechanical contact with a strong permanent magnet, which magnetized both outer garnet layers into the same saturated state, after which these layers’ magnetization was at its remnant (monodomain) state. The image thus only revealed the magnetic domain pattern of the intermediate (magneto-soft) layer.
Fig. 4.25 Magnetic domain patterns observed in an all-garnet multilayer thin-film structure onto a GGG substrate (deposited at $T_{\text{sub}} = 250 \, ^\circ\mathrm{C}$ and subjected to anneal at 630 °C for 3 h) using a transmission-mode polarization microscope at high magnification (630 X).

The experimental results achieved in multilayer structure demonstrated the possibility of engineering the magnetic properties of multilayer all-garnet structures using combinations of materials with different magnetic behaviour types. It has been discovered that it was possible to modify the magnetic properties of garnet materials with a goal of reducing the coercive force whilst maintaining high specific Faraday rotation and remanence by making all-garnet multilayer structures, which is technologically interesting for a number of applications in photonics and integrated optics. These types of nano-engineered garnet multilayer structures are very important for multiple applications in nano-photonics, especially for the design of optical sensors and integrated optical isolators.

### 4.5 Summary

The fabrication process parameters including the deposition and annealing process of Bi-substituted iron garnet and garnet-oxide composites (having different volumetric concentration of $\text{Bi}_2\text{O}_3$) of different magnetization behaviour have been discussed and the best achieved results in terms of optical and MO properties in these materials have been described. The annealing effects on the properties of these materials will be explained in next chapter. The micro-structural properties of garnet (single layer) thin films have also been described in this chapter. The characterisation results of a garnet multilayer thin film structure (proposed to engineer the magnetic properties often not possible to achieve in a single thin garnet layer) have been discussed, and the material properties achieved are shown to be very attractive for various devices and applications in magneto-optics and photonics.
CHAPTER 5

ANNEALING BEHAVIOUR AND MO PERFORMANCE OF CO-SPUTTERED NANO-COMPOSITES BASED ON Bi-SUBSTITUTED IRON GARNETS AND BISMUTH OXIDE

Introduction

This chapter describes the experimental study of the annealing behaviour of garnet-oxide composite thin-film materials and the effects of isothermal annealing treatment on the properties of highly bismuth-substituted iron garnet materials. The evolution of the optical and magneto-optical properties of garnet films of composition type \((\text{Bi, Dy, Lu})_3(\text{Fe, Ga, Al})_5\text{O}_{12}\) and the study of kinetics of garnet phase formation within a garnet-Bi-oxide nano-composite material of type \((\text{Bi, Dy})_3(\text{Fe, Ga})_5\text{O}_{12}: \text{Bi}_2\text{O}_3\) are discussed in this chapter.

5.1 The approach of nanocomposites synthesis

Numerous investigations have been performed to find the relationship between the MO properties (Faraday rotation) and the Bi-content of various garnet-type material systems. A strong dependence of Faraday rotation (FR) on the number of bismuth atoms per formula unit in the thin-film materials was documented in garnet films prepared by liquid-phase epitaxy (LPE), as reported in Ref. [3]. A linear growth of specific FR with increasing bismuth content has been demonstrated in LPE films prepared by making compositional changes from \(\text{Lu}_3\text{Fe}_5\text{O}_{12}\) to \(\text{Bi}_{2.4}\text{Lu}_{0.6}\text{Fe}_5\text{O}_{12}\) which is an LPE film of record-high Bi-content. It was also observed that a smaller than expected Bi-substitution levels were normally achieved in sputtered thin films of composition type \((\text{Bi, Dy/Lu})_3(\text{Fe, Ga/Al})_5\text{O}_{12}\). In order to investigate the source of such disagreement and also to increase the number of bismuth atom introduced into the garnet structure, a number of \((\text{Bi, Dy/Lu})_3(\text{Fe, Ga/Al})_5\text{O}_{12}: \text{Bi}_2\text{O}_3\) nano-composite materials were synthesized using RF co-sputtering technique, and we demonstrated composite garnet-oxide films of very high MO quality. The additional \(\text{Bi}_2\text{O}_3\) target worked as a source of excess bismuth atoms for the garnet films of the same composition type, as was confirmed by the XRD characterization data (Chapter 4).

Highly Bi-substituted MO garnet and garnet-oxide composite films of amorphous structure (as-deposited films) have been subjected to crystallization to obtain the garnet
phase and achieve polycrystalline microstructure within the garnet layers [56, 116]. Note that finding an optimized annealing regime for each garnet thin film material type was always a key factor necessary to achieve the best optical and MO properties in films, as well as to maintain high quality film surfaces. The annealing temperatures and process durations used to crystallize a range of garnet-Bi-oxide composite garnet layers have been experimentally optimized in order to study the annealing behavior of garnet-oxide composite films. The effects of annealing heat treatment running with different temperatures and process durations on the optical and MO properties of garnet thin films of both types have been observed and evaluated to investigate the ways of optimizing the relevant process parameters, as well as the crystallization kinetics of a class of co-sputtered garnet-oxide materials of type (Bi,Dy)₃(Fe,Ga)₅O₁₂: Bi₂O₃. The study of crystallization kinetics (amorphous to crystal phase transformation) of the garnet-oxide composites undertaken revealed important information on the annealing behavior of these materials. A significant number of research works have been conducted to crystallized rare-earth iron garnet materials including Bi-substituted iron garnets using different thermal annealing processes. [65,117-125]. The garnet-bismuth oxide composite materials of composition type (Bi,Dy)₃(Fe,Ga)₅O₁₂: Bi₂O₃ possessed record-high MO figure of merit, simultaneously, with magnetic memory properties only after being crystallized with the optimized annealing process [23].

5.2 Design and optimization of annealing regimes

A large number of co-sputtered garnet-oxide composite layers of different thickness as well as the typical garnet layers from several different deposition batches were annealed using a range of crystallization temperatures between 480-700 °C and different process durations. The evolution of the optical, magneto-optic and also the microstructural properties of garnet-oxide composite layers with increasing thermal exposure were observed. It was found that garnet-oxide composites had a particularly narrow “thermal processing windows” in terms of both the annealing temperature and process durations suitable for achieving the best possible MO figure of merit in each material type. The experimental study and the analysis of annealing garnet materials typically revealed that it is often possible to either “under-anneal” or “over-anneal” the films, thus obtaining the samples with either the non-optimal specific Faraday rotation, or the surface damage/material degradation leading to significant scattering of transmitted light, or exhibiting a combination of these effects. Fig. 5.1(a) shows the “processing window
Fig. 5.1 (a) Approximate boundaries of the annealing temperature regimes found to be suitable for the crystallization of two types of high-performance garnet-oxide composite films defined by the stoichiometry (Bi,Dy)$_3$(Fe,Ga)$_5$O$_{12}$: Bi$_2$O$_3$ with different volumetric quantities of co-sputtered bismuth oxide content; (b) summarized data of annealing temperatures used to crystallize Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ and two batches of Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ composite layers having 4.5 and 12.5 vol. % extra bismuth oxide deposited onto GGG (111) substrates.
Running the annealing processes at or below the “lower boundary” temperatures would lead to obtaining only very small specific Faraday rotations after 1 hour-long process durations. Running the annealing processes at or above the indicated “upper limit” temperatures will very likely lead to material decomposition and/or significant film surface degradation and the formation of large pores within the films’ volume. The analysis of isothermal annealing behavior of garnet-oxide composites was limited to the conventional oven annealing processes, in which isothermal crystallization was achieved at the “annealing temperatures” and the temperature-ramp processes were run at a constant rate of 5 °C/min. Since the absolute accuracy of temperature control achievable in the box-furnace oven type was estimated about ± 5 °C, the “annealing process duration” was counted adding two minutes with the duration of the isothermal crystallization process, in order to account for the effects of the last minute of the temperature ramp-up process and the first minute of the temperature ramp-down process.

On the other hand a range of annealing temperatures between 530-680 °C were used for different annealing durations to crystallize the as deposited garnet layers (amorphous phase) and garnet-oxide composite films of composition type $(\text{Bi}_{3} \text{Lu}_{3})_{5}(\text{Fe}_{3} \text{Al})_{5} \text{O}_{12}$. For this type of garnet material it was found that the optimum annealing temperature window becomes narrower with the increase in the amount of extra bismuth oxide content compared to that for the typical garnet layer of same composition. The annealing process duration regimes were found to be much higher than that used to anneal the other garnet composition type. The effects of optimized annealing regimes on the optical and MO properties of garnet-oxide nano-composite materials have been studied and the materials’ performances evaluated. The annealing experiments were subjected to the sample-to-sample and batch-to-batch and achieved almost repeatable results in annealed material properties.

The optimum annealing regimes of garnet-oxide composite films were found to be extremely composition-dependent. The optimization of the annealing regimes is not only the key for obtaining good optical and MO properties in garnets and garnet-oxide composites, but is also crucial for obtaining the high-quality microstructure and surfaces in garnet layers. A summary of microstructural properties obtained in garnet-oxide
The microstructural properties of several garnet-oxide composite films of type (Bi,Dy)$_3$(Fe,Ga)$_5$O$_{12}$: Bi$_2$O$_3$ having different vol. % content of excess bismuth oxide have been characterized to observe the modification of the microstructural properties of the garnet-oxide composite layers occurring during the thermal process. Fig 5.2 (a) shows an over-annealed composite film having est. 17% of added Bi$_2$O$_3$ deposited onto GGG (111) substrate, annealed for 2 hrs @ 620 °C and later re-annealed for 1h at 700 °C having large grains while (b, c) shows the films (under-annealed and over-annealed) deposited onto Corning 7059 substrate having an est. 30 vol. % and 33 vol. % of added Bi$_2$O$_3$ and annealed at different annealing regimes, possessed indistinguishable microstructure from that of an amorphous layer and bubble-like features throughout film volume respectively. A high-MO-performance composite film (slightly over-annealed, having nano-scale porosity features about 50 nm feature size) having 24 vol.

Fig. 5.2 SEM and ion-beam microscope cross-sectional images of several garnet-oxide composite films of types Bi$_2$Dy$_3$Fe$_4$Ga$_1$O$_{12}$: Bi$_2$O$_3$ (images a-c) and Bi$_2$Dy$_3$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (image (d)) annealed using different process regimes. The SEM images (a-c) are courtesy of Young-Min Song, Gwangju Institute of Science and Technology, Korea. The ion-beam image (d) is that of an FIB-prepared cross-section of our MO film coated with 20 nm of silver and a platinum (Pt) protective layer to enable imaging [108].

composite films of type (Bi,Dy)$_3$(Fe,Ga)$_5$O$_{12}$: Bi$_2$O$_3$ are shown in Fig. 5.2. The annealing regimes (both temperature and process duration) were experimentally optimized for the crystallization of a range of Bi-substituted iron garnet-oxide films.
% of excess Bi$_2$O$_3$ deposited onto GGG (111) substrate and annealed for 1 h at 580 °C (Fig 5.2(d)). The annealing regimes used for this film was slightly higher than was exactly needed for this composition to be annealed according to the best thermal processing regime found for this material and possessed excellent crystalline material properties, high Faraday rotation as well as the MO quality.

5.3 Measurement and characterization of optical properties

A series of annealing experiments have been performed with a large batch of garnet-oxide composite films of type Bi$_2$Dy$_{1.5}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17±2 vol. %) at the process temperatures of 550°C, 560°C and 570°C, for a number of different annealing durations, and the evolution of the optical and magneto-optical properties studied. The presence of large specific Faraday rotations observed in highly Bi-substituted garnet compounds in the visible spectral range characteristic confirmed the crystallization of garnet-oxide composite samples performed using correct annealing regimes with the conventional oven annealing system. However, among the numerous samples, some had very large Faraday rotation but possessed high optical absorption and some samples had lower-than-expected specific Faraday rotation and low optical absorption. Figure 5.3 shows the evolution of the absorption coefficient spectra of films type Bi$_2$Dy$_{1.5}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17 vol. %) sputtered onto GGG (111) substrates occurred during annealing at 560 °C with the increasing annealing process duration and compared with those obtained in the materials of the same composition of amorphous layer and annealed at different annealing regimes. The data shown in Fig. 5.1 illustrates that the optimization of the annealing process duration and temperature was essential for achieving the low-absorption performance of garnet-Bi-oxide composite films. A range of annealing temperatures between 550-570 °C were found to be the optimum temperature regime to crystallize the thin film materials sputtered onto both glass and GGG substrates and the optimum range of annealing process durations was found to be between 15-45 minutes (at 560 °C). Note that similar trends of absorption spectra behaviour have been observed in all co-sputtered garnet-oxide materials (up to the excess bismuth oxide fractions of about 49 vol. %). The samples sputtered onto glass substrates sometimes showed higher optical loss than that of the samples prepared onto a paramagnetic transparent substrate GGG (111).
Fig. 5.3 Derived absorption coefficient spectra of garnet-bismuth-oxide composite films of composition type Bi$_2$Dy$_4$Fe$_4$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17 vol. %) from the same batch of samples (deposited onto GGG (111) substrates) after being subjected to different thermal processing treatments. The specific Faraday rotation values of all annealed films measured using 532 nm light are shown, as well as the absorption spectrum of the same material in the amorphous phase [108].

The nano-composite films of type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ having excess of bismuth oxide (up to 20 vol. %) were also subjected to annealing using a range of temperatures between 610-680 °C for different annealing process durations. Significantly, lower absorption coefficients were obtained in garnet-oxide composite films across the visible spectral region compared to the typical Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$ garnet layers (Fig. 4.13, Chapter 4). To study the effects of annealing on the optical and MO properties of this material composition, a particular batch of garnet-oxide composite films (Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ having 4.5 vol. % excess Bi$_2$O$_3$) were annealed using the isothermal oven-annealing system. It was found that the optimized annealing temperatures were between 610-620 °C and the optimized time duration varied between 3-20 hours. Significant effects of the annealing temperature on the optical properties are summarized in Fig. 5.4 in terms of optimized spectra of absorption coefficient achieved in Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. % of excess Bi$_2$O$_3$) garnet-oxide composite films sputtered onto GGG (111) substrates and annealed at 610-620 °C for different annealing time durations up to 20 hours.
Fig. 5.4 Derived absorption spectra of Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol%) composite on GGG (111) annealed at 610°C and 615°C for different annealing process durations; the measured Q-factors at 532 nm and 635 nm are indicated.

The same trends of optical absorption spectra were also observed in this composition prepared onto the glass substrate (Corning Eagle XG) that leads to achieve high MO figure of merit (MO quality factor).

5.4 Evaluation of MO properties

The measured data points of specific Faraday rotation and the MO figure of merit (quality factor) at 532 nm of garnet-Bi-oxide composite films of composition Bi$_3$Dy$_{1}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17 vol. %) from the same batch (Fig. 5.3), sputtered onto glass substrates are shown in Fig. 5.5. There were two common observations found for all the oxide-mixed films (sputtered onto both glass and GGG substrates), annealed at 550-570 °C. Firstly, in all experiments, the specific Faraday rotation of films quickly changed from negligibly small values to almost their maximum-observed values after short process durations in any given material type with small changes in the annealing process duration and secondly, the specific Faraday rotation of films seemed to reach its maximum value and then remained almost constant, but within a limited time interval only, after which a trend of slow decrease in the specific Faraday rotation was observed. The MO figures of merit have always peaked almost simultaneously with the observed peaks in the specific Faraday rotation, after which, a slight yet notable decreasing MO
quality trend was observed, finally leading with the increasing process durations towards some nearly-identical, but sub-optimal MO figures of merit.

![Graph showing specific Faraday rotation and MO figure of merit evolution with annealing duration.](image)

Fig. 5.5 Measured evolution of the specific Faraday rotation and MO figure of merit at 532 nm with increasing annealing durations for films of Bi$_2$Dy$_2$Fe$_4$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17±2 vol. %) deposited onto Corning 1737 glass substrates.

Very similar trends in the annealing behavior have been observed in garnet-Bi-oxide composite films of this composition deposited onto GGG substrates. The decreases of optical (surface degradation) quality as well as the specific Faraday rotation was observed with the increase of annealing process durations. It was due to the possible formation of non-garnet material phases and large pores within the films’ volume, or the stress-induced microcracks propagation. More attention is needed to optimize the isothermal annealing treatment to achieve substantially maximum possible MO figure of merit with high quality film surface in each material type (sputtered onto both GGG and glass substrates). Note that the surfaces of the films deposited onto GGG substrates were much more “microcrack-free” after annealing treatment than these of films deposited onto glass substrates. This was due to smaller differences in thermal expansion coefficients between garnet-Bi-oxide composite layers and garnet substrates.

Fig. 5.6 shows the summary of the optimization results for the annealing regimes used to crystallize the garnet and garnet-oxide amorphous layers and also the values of best-
achieved MO figures of merit (data points measured using a 635 nm plane-polarized laser source). These are reliable sources of data to reproduce high bismuth content garnet thin films of composition type \((\text{BiLu})_3(\text{FeAl})_5\text{O}_{12}\).
oxide composite films of composition Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. % extra bismuth oxide).

Fig. 5.7 Measured MO figure of merit in composite film of composition type Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.6}$Al$_{1.4}$O$_{12}$: Bi$_2$O$_3$ (4.5 vol. %) annealed at 610 °C and 615 °C for different annealing process durations. It revealed the necessity to find optimized annealing process duration as the values of MO figure of merit decreases with the increase of process time after the optimized annealing time has been reached.

5.5 Kinetics of garnet nanocrystals formation within the garnet-Bi$_2$O$_3$ nanocomposites

The obtained results (optical and MO properties) in the garnet-oxide composite films of type Bi$_2$Dy$_{1}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17±2 vol. %) after the annealing process conducted at the temperatures of 550 °C, 560 °C and 570 °C with different annealing durations were studied and analysed to characterize the crystallization kinetics of this material type. The crystallization kinetics with an estimation of activation energy of crystallization for oven-annealed epitaxial garnet films described in [9]. The time- and temperature dependencies of the extent of crystallization of the garnet-oxide composite film have been analysed and it was found that these analyzed results satisfy the Avrami equation [126, 127] and Arrhenius law for isothermal crystallization [127-130]. The activation energy of isothermal crystallization of Bi-substituted iron garnet materials were found to be rather large, which explains the observed narrowness of the “thermal processing windows”. The amorphous (as-deposited) to nanocrystalline phase transformation kinetics was studied using the samples with high-quality surfaces (except in some over-annealed films), and good optical and MO properties.

Since the conventional oven annealing processes induce the temperature-activated isothermal crystallization of amorphous (as-deposited) garnet layers, it is of interest to
quantify the activation energy of these crystallization processes, as well as analyse the process kinetics and the dependency of the optimum annealing parameters on substrate type. The approach described in Refs. [127-130] has been considered and applied for this analysis. It is well-known that the kinetics of thermally-activated processes (including the case of garnet crystallization being considered) follows a dependence on temperature described by the Arrhenius law (Eq. (5.1)): 

$$K = K_0 \exp\left(-\frac{E_c}{kT}\right),$$

(5.1)

where $K$ is the rate constant of the crystallization process, $K_0$ is termed the pre-exponential factor, $E_c$ is the activation energy of crystallization, and $k$ is the Boltzmann constant. During the isothermal phase change, the extent of crystallization $A$ of a material is described by the Avrami’s equation (Eq. (5.2)) [13]:

$$A(t) = 1 - \exp[-(K^*t)^n],$$

(5.2)

where $t$ is the process duration, $K$ is the crystallization rate constant, and $n$ is the order parameter dependent on the crystal growth mechanism.

The extent of crystallization measurements of sputtered garnet-oxide composite films composition type $\text{Bi}_2\text{Dy}_1\text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12}: \text{Bi}_2\text{O}_3$ (17±2 vol. %) have been performed for three different annealing temperatures. The extent of crystallization was quantified as the ratio of the specific Faraday rotation measured in films after running any given annealing process, to the maximum specific Faraday rotation at the same wavelength (we used 532 nm and 635 nm light) achieved in any given material/substrate system after running the process at the same annealing temperature with the “best-known” parameters. All specific Faraday rotation data obtained from film samples deposited onto GGG substrates were measured in the remnant magnetization states, in order to exclude the paramagnetic effects of 0.5 mm-thick GGG substrates which led to measuring slightly increased Faraday rotation angles when placed in the electromagnet’s field of up to 2.5 kOe. For samples deposited onto Corning 1737 glass substrates, Faraday rotation data was taken at the saturation magnetization, even though all films maintained about 90% of Faraday rotation after being removed from electromagnet. The physical thicknesses of the garnet layers were determined for each
sample using software-assisted fitting of the measured transmission spectra to the theory-predicted spectra using the measured data for the dispersion of the refractive index and absorption coefficients, as reported in [23, 74]. Since the annealing behaviors of garnet films sputtered onto GGG (111) and Corning 1737 glass substrates were, *apriori*, known to be different, the data for samples of different substrate types were processed separately. The data analysis strategy used to derive the Arrhenius equation parameters of this garnet material followed the approach described in detail in [128-130]. Fig. 5.8 illustrates a typical relationship between the measured extent of crystallization and the annealing time (a sigmoid-shaped crystallization curve).
Fig. 5.8 Measured relationships between the extent of crystallization (A) and the annealing time (isothermal crystallization process duration) for garnet-oxide composite films of type Bi$_2$Dy$_{1.3}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17±2 vol.%) sputtered onto (a) GGG (111) and (b) glass (Corning 1737) substrates and annealed for different time durations at 550 °C.
Fig. 5.9 Plots of $\ln[\ln(1/(1-A))]$ vs $\ln(t)$ for $\text{Bi}_2\text{Dy}_1\text{Fe}_{2.3}\text{Ga}_{0.7}\text{O}_{12}$: $\text{Bi}_2\text{O}_3$ (17±2 vol.%) composite films sputtered onto monocrystalline GGG (111) substrates and annealed for different time intervals at (a) 550 °C, (b) 560 °C and (c) 570 °C. The data points considered “outliers” and/or “over-annealed” are shown within dashed circles.
Fig. 5.10 Plots of \( \ln[\ln(1/(1-A))] \) vs \( \ln(t) \) for Bi\(_2\)Dy\(_{1.3}\)Fe\(_{4.3}\)Ga\(_{0.7}\)O\(_{12}\): Bi\(_2\)O\(_3\) (17±2 vol.%) composite films sputtered onto Corning 1737 glass substrates and annealed for different time intervals at (a) 550 °C, (b) 560 °C and (c) 570 °C. The “outlier” or “over-annealed” data points are also shown, as well as least-squares linear regression fitting results.
Avrami plots of $\ln[\ln(1/(1-A))]$ versus $\ln(t)$ were studied to reveal the values of crystallization order parameters and also these of $\ln(K)$. Avrami plot results for films deposited onto both substrate types annealed at different temperatures, together with the lines fitted by the least-squares regression, are shown in Figs. 5.9 and 5.10. The data points generated using measurements performed with 635 nm light are shown in red and the points measured using 532 nm light are shown in green. The “outlier” or “over-annealed” data points not used in the regression fitting are also shown within dashed circles. All time durations were measured in minutes. The slopes and the intercepts of the plots of $\ln[\ln(1/(1-A))]$ vs $\ln(t)$ (Figs. 5.9 and 5.10) reveal the (approximate) values of the crystallization order parameters and also these of $\ln(K)$ at each process temperature.

According to the Arrhenius expression (Eq. (5.1)), the crystallization rate constant is a function of temperature, and it is well-understood that it depends on both the nucleation and growth rates of the new phase. Annealing at higher temperatures increases the growth rate substantially, but studies of crystallization at temperatures above 570 °C could not be carried out due to the oven temperature controller’s limitations. On the other hand, annealing at low temperatures (in our case, below 550 °C) was not productive due to the very slow crystallization rates, which could mean that weeks or even years of annealing would be required to transform the amorphous-phase materials into polycrystalline phase.

For thermally-activated isothermal crystallization processes, the Arrhenius equation shows that the crystallization rate constant is significantly temperature-dependent, and the obtained linear-regression straight-line fits of the $\ln(K)$ vs $1000/T$ data points suggest the applicability of Arrhenius law to the process considered. The slopes of fitted lines shown in the Arrhenius plots of Fig. 5.11 are defined by the activation energy of crystallization, whilst the intercepts can be used to reveal the value of the pre-exponential factor of the crystallization process ($\ln(K_o)$). Only three temperature data points were used due to the narrowness of the thermal processing window suitable for the material type selected, and because we utilized only (a limited number of) material samples from a single deposition batch. Therefore, any material composition uncertainties arising out of batch-to-batch repeatability were excluded. Using Eq.(5.1)
and the fitted regression slope values shown in Fig. 5.11, the following estimates of the activation energy of crystallization were obtained: 14.99 eV for films deposited onto GGG substrates and 15.6 eV for films deposited onto Corning 1737 glass substrates; both values were estimated to about ±10% accuracy. It is important to note that the activation energy values obtained from our estimates were much larger than those expected for simple diffusion-driven processes. This might indicate that diffusion and also nucleation/growth mechanisms as well as interface processes may affect the overall kinetics of the rather complex crystallization process, as described by the authors of [130].

Fig. 5.11 Arrhenius plots of ln(K) vs 1000/T for Bi$_2$Dy$_{1}$Fe$_{4.3}$Ga$_{0.7}$O$_{12}$: Bi$_2$O$_3$ (17±2 vol.%) composite films sputtered onto (a) GGG (111) and (b) Corning 1737 glass substrates.
The optimization of annealing regimes used for this material type $\text{Bi}_3\text{Dy}_1\text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12}$, $\text{Bi}_3\text{O}_3$ (with est. (17±2) vol. % of excess bismuth oxide) enabled some improvement in the MO figures of merit (as measured in the visible range) and found a strong agreement with the results previously achieved for this material type and described in chapter 4. The study of crystallization kinetics undertaken with a sample batch of such garnet-oxide composite material has yielded important process-related information and data, including the estimates of the activation energy of isothermal crystallization. These experimental data are not sufficient to explain in every detail the ways in which the phase transformation (amorphous to crystal-phase) occurs during the annealing treatment, and also not enough to calculate the precise activation energy of crystallization for the MO garnet thin film materials. According to the best of my knowledge, there was also not enough data and a few reports only found so far in the literature in relation to the studies of the crystallization kinetics in garnets. This experimental work was an attempt to study the annealing behaviour as well as the kinetics for the highly Bi-substituted iron garnets. The crystallization process studies were conducted by performing multiple annealing experiments for garnet films using different annealing time/temperature regimes (within the optimized annealing temperatures ranges found suitable for the annealing of as-deposited garnets of the specified composition types) which took more than a couple of months during my study period, when I performed the characterization experiments with multiple annealed film batches to describe the optical (transmission and absorption) and also MO (specific Faraday rotation) properties of all garnet samples trialled. I believe that the obtained results can be used as a guide for obtaining high-performance MO films and also to design optimized thermal processing regimes suitable for the crystallization of magneto-optic garnet materials of the described type.

5.6 Summary

The effects of annealing temperature and process duration variations on the optical and MO properties of $(\text{Bi, Dy/Lu})_3(\text{Fe, Ga/Al})_5\text{O}_{12}$ garnet materials have been observed and their performances evaluated, the crystallization kinetics of Bi-substituted iron garnet composites (of the composition type $\text{Bi}_3\text{Dy}_1\text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12}$, $\text{Bi}_3\text{O}_3$) has also been studied and an estimated activation energy of crystallization for this type of garnet materials has been calculated. The improved properties of these garnet materials achieved by using the best-identified annealing regimes make them even more attractive for various
applications in integrated optics and photonics, and some of the emerging applications of these materials are also identified and explained in Chapter 6.
CHAPTER 6

APPLICATIONS OF SPUTTERED GARNETS AND GARNET-OXIDE NANOCOMPOSITE FILMS IN IMAGING, SENSING AND INTEGRATED OPTICS AND PHOTONICS

Introduction

Modern civilization demands superior technologies and high-speed communication systems for achieving lifestyle improvements. It is the challenge for modern science and technology to serve the requirements of society by providing all required technological facilities and also innovative functional materials through new research, inventions and through the reconfiguration of existing devices and technologies. With the engineering of novel synthesized magneto-optic materials there are many possibilities for growth in the application of these materials. In this chapter, the potential application areas of our newly engineered nanocomposite materials requiring the functionalities based on Faraday effect and magnetic memory are discussed.

6.1 Nano-structured MPCs for MO polarization controllers

Bi-doped iron garnet materials possess the highest Faraday rotation per unit film thickness of all semi-transparent optical materials, a substantially low optical absorption at the communication-band wavelengths, and can demonstrate record-high magneto-optic (MO) figure of merit. The combination of excellent properties (obtained in newly synthesized Bi-substituted metal-doped iron garnets) makes them highly attractive for use as magnetic components of MPC structures. Nowadays magnetic photonic crystals (MPC) are one of the numerous emerging types of nano-structured media receiving substantial research interest. MPCs can provide new and unique functionalities for the design and development of nano-scaled integrated optics components and systems as an example polarization controller. Control over the state of polarization of light waves is extremely important for a range of applications, including the development of laser- and fibre-based optical sensors, optical communications hardware, lightwave measurement and characterization systems [17-19, 83, 84, 106, 107, 131].

MPCs are the periodic or quasi-periodic sequences of magnetic and non-magnetic materials incorporated into photonic crystal-type systems, and these can lead to several new optical phenomena and can give rise to the substantial enhancement of
conventional magneto-optical (Faraday, Kerr, Voigt) effects [83, 106, 131]. MPCs can be designed as all-garnet heterostructures typically composed of ferrimagnetic and transparent paramagnetic garnet materials with/without any defects within the layer sequences. A schematic diagram of a typical MPC structure described by a multidefect structural formula \((MN)^a (NM)^b (MN)^c \ldots (NM)^z\) is shown in Fig. 6.1, where M and N represent the magnetic and nonmagnetic constituents.

![Schematic diagram of a typical MPC structure](image)

**Fig. 6.1** Typical structure of a magneto-photonic crystal (MPC) with phase shifts. A sequence of magnetic (M) and non-magnetic (N) layers forms a quasi-periodic 1-D photonic crystal structure. Externally applied magnetic field \((H)\) directed along the light propagation path allows control of the photonic bandgap properties and polarization state of light transmitted through MPC.

The properties of an optimized 1-D MPC of structural formula \(S(N_1N_2)^{10}(MN_2)^1(MM)^{14}(MN_2)^1(N_2N_1)^10\) where \(N_1\) and \(N_2\) represent the non-magnetic materials and M is the doped iron garnet layers as magnetic constituents have been investigated for use in integrated-optics polarization controllers [82]. An optimized MPC structure was modelled and characterized using an efficient Window-based C++ algorithm based on the \(4\times4\) transfer matrix method, which allows evaluation of all possible design variations suitable for the structure manufacture with a given set of several different material types. The predicted performance (transmission, reflection and Faraday rotation spectra) of an optimized 1-D MPC structure containing bismuth- and gallium-doped dysprosium iron garnet compounds as magnetic constituents of MPC and GGG and TiO\(_2\) as non-magnetic constituents is shown in Fig. 6.2.
Fig. 6.2 Predicted Transmission (a) and Faraday rotation (b) spectra of the structure \( S(N_1N_2)^{10}(MN_2)^{1}(MM)^{14}(MN_2)^{1}(N_2N_1)^{10} \) composed of 43 deposited layers and having a total thickness of 12.72 \( \mu \)m (the gyration value used in modelling was - 0.001i) designed to generate in excess of \( \pm 31^\circ \) of Faraday rotation for the transmitted light near 1550 nm.

We engineered the enhancement of Faraday rotation near 1550 nm and describe a novel hysteresis-based driving scheme based on magnetic hysteresis loops with memory observed in the Bi-substituted Ga-doped MO garnet materials, suitable for implementing ultra-fast polarization controllers for various applications in telecommunication, sensing and measurement systems. The magnetization states of
MPC can be controlled due to having uniaxially-anisotropic garnet material with remnance properties inside the entire MPC structure. The remnant magnetization states of MPC can be brought to any value between its two oppositely-magnetized saturation states by means of applying sequentially two very short current pulses. The short current pulses of 10-50 ns can switch the Faraday rotation angle to any angle between the two range-limiting states. Fig. 6.3 shows a schematic diagram of the hysteresis loop of Faraday rotation utilizing the minor hysteresis loops which is a new concept of controlling polarization direction of light propagating through MPC in a wide range, limited by the magneto-optic quality factor of the magnetic nanostructures.

![Fig. 6.3 Schematic diagram of magnetic hysteresis loops including minor loops, where the minor loops show the control over the remnant state of magnetization with the very short current pulses that provides the possibility to control the polarization direction of the light propagated through the photonic crystals.](image)

A number of process parameters critically need to be optimized to successfully manufacture MPC structures providing the significant MO quality including garnet material selection, crystallization of garnet materials and also the simultaneous crystallization of different garnet layer types within the heterostructures. Newly synthesized Bi-substituted iron garnet of composition type (BiDy)$_3$(FeGa)$_5$O$_{12}$ having high MO quality factor and strong uniaxial magnetic anisotropy with the direction of the
easy magnetization axis being perpendicular to the film’s plane is suitable to use as the magnetic constituent of MPC structures. Optimization of processes parameters to crystallize single garnet layer and also the simultaneous crystallization of different garnet layer types within the heterostructures were studied and performed in this research work, provides a significant opportunity to successfully manufacture MPCs suitable for the practical applications. Fig. 6.4 shows a XTEM micrograph of a tri-layer all-garnet coating of structure GSGG/Bi2Dy1Fe4Ga1O12/GSGG on a GGG substrate simultaneously crystallized with two paramagnetic garnet layers which is an elementary building block of MPC structures [56]. The crystallization behaviour of this heterostructure represented by a ferrimagnetic garnet layer surrounded by two paramagnetic garnet layers shows that the garnet grains of a relatively spherical shape are tightly packed (almost without voids) within the surrounding layers.

Fig. 6.4 Bright-field XTEM micrographs of a garnet tri-layer coating of GSGG/Bi2Dy1Fe4Ga1O12/GSGG on a GGG (111) substrate showing the microstructure changes and the interface layers between the different garnet materials [56].

The highly promising and world’s best MO figures of merit achieved in this type of garnet films across the visible spectral range (described in Chapter 4) make them extremely attractive for use in nano-structured magneto-photonic components as well as MPC-based devices. Though it is difficult to precisely measure the MO figures of merit of garnets in the communication-band range, due to the extremely low absorption coefficients, we expect these figures to be in excess of several thousand.

The nearly “square” hysteresis loops of Faraday rotation obtained in various garnet film samples (Fig 4.10 in Chapter 4 demonstrated different coercivities and switching fields) provide the possibility of controlling the polarization direction of plane-polarized light waves. Substrates dependent field of coercivity and the dynamics of magnetization
switching process were observed in these garnet films. Fig. 6.5 shows the hysteresis loop of Faraday rotation measured in a garnet film of 0.85 µm thickness showing the “return paths” from several different magnetization states illustrate the feasibility of ultra-fast magnetic field driven polarization control devices that can be developed using this type of garnet films and MPCs.

By means of two consecutive short current pulses of duration 20-50 ns it is possible to completely control the state of polarization of a plane polarized light wave transmitted through such Faraday rotators. A sufficient magnetic field will be generated into the integrated system (MPC integrated with micro-coil) by the first pulse of the applied short current. This magnetic field will bring all magnetic constituents of an MPC structure into one of its saturation magnetization states from any arbitrary magnetization state. The second (opposite polarity) smaller-current pulse will then bring the system into any desired remnant magnetization state existing on any chosen minor hysteresis loop, between the two range-limiting “principal” remnant states that belong to the major hysteresis loop. Thus, it is possible to quickly switch the Faraday rotation angle of light
transmitted through MPCs to any value between the two range-limiting maxima with a suitable calibrated peak of second current pulse.

This work towards the fabrication of magneto-photonic crystals is an ongoing research effort, and some works have been conducted during the establishment of highly bismuth substituted iron garnet and garnet-oxide composites as a building block of proposed MPC structure. The preliminary results obtained in 3-5 layers multi-structures having magnetic and non-magnetic materials (results are not published anywhere by this group) indicates that it is possible to manufacture such kind of MPCs which will allow to control the state of light polarization across the telecommunication wavelength.

6.2 High-contrast MO imaging for security and digital forensics

The magneto-optical investigation techniques are usually based on the Faraday effect which requires either transparent or semi-transparent thin film materials with large Faraday rotation. Bi-substituted iron-garnet thin films are very promising magneto-optic (MO) indicator films that can visualise the magnetic leakage fields generated by magnetised objects in situations requiring non-destructive evaluation, can measure magnetic flux distributions in superconductors, or image magnetic patterns on audio tapes and digital disks [43, 77,132]. MO thin films visualization opens the possibility of overcoming the barriers that exist with current and most commonly used techniques (Magnetic Force Microscopy (MFM) and magnetic force Scanning Tunnelling Microscopy (STM)) for imaging the magnetisation patterns with high resolution [133-137].

The basic principle of MO imaging and visualisation technique using garnet thin films is illustrated in Fig. 6.6, where polarised input light is used in conjunction with a nano-engineered magnetic field imager. Sub-micron spatial resolutions, capable of magnetic hard drive data imaging, can be attained if UV or blue-range visible light sources are used.
The MO imager film (Bi-substituted dysprosium iron garnet) is placed very close to the surface of the disk being imaged (this “flying distance” needs to be of the order of the bit size, \(\sim 100\) nm), and this is technically feasible, especially because the nano-structuring of the ultra-thin films (single layer or multilayer) can reduce the switching magnetic fields to below 100 oersted (Oe). The magnetic structures of the data recorded on the media are imprinted into the MO thin films and are memorised by the films, allowing post-processing of the captured data distributions, as well as transmission-mode imaging. Moreover, due to the advantage of the low Curie temperature \((T_C)\) of the magneto-optical materials (\(\sim 180^\circ\)C), the coercive force reduces significantly by heating the visualiser to above \(T_C\) just before placing them in close proximity with the disk surface. After cooling the thin film, the data is memorised by the thin-film visualizer for later imaging and processing.

The data bits recorded onto the magnetic medium under investigation generate a stray magnetic field that magnetises the MO imager film layer and latter rotates the polarisation of the input light by an angle which depends on the data recorded. An
output analyser, set near the extinction condition with respect to the input light polarisation, generates a magneto-optic image of the data tracks. However this MO imaging process will be more effective and easy to handle for the typical user to recover the data stored in ultrahigh-density magnetic media over those existing techniques.

Highly Bi-substituted dysprosium doped iron garnet possessed large Faraday rotation, low optical loss, excellent crystallinity and very small grain (crystallite) size as well as submicron-scale magnetic domain sizes. The magneto-optic imaging mechanism is critically dependent on the domain size of the garnet thin films, since each magnetic domain is essentially used as a “bit” in the digital-type compound images obtainable after being brought into the close proximity of the magnetised object under study. The excellent remanence (magnetic memory properties) of the garnet films makes it possible to permanently imprint the images of bits recorded onto almost any perpendicularly-magnetized magnetic medium into the films magnetic domains patterns. Figure 6.7 shows the imaging results of the magnetic media data patterns achieved using a brief mechanical contact of Bi-substituted iron garnet nanocomposite films with these media and later revealed using polarization microscopy. Visible-light polarisation microscopy was used to generate images (a, b) and UV (365 nm) polarisation microscopy was used to generate images (c, d). Using short-wavelength (UV) illumination, it is possible to achieve imaging resolutions suitable for working with high-density storage media whilst staying within the Rayleigh limit.
Fig. 6.7 Transmission-mode polarising microscope images of (a) data tracks recorded on a 3.5” (1.44 MB) HD floppy disk; (b) magnetic patterns of a credit card obtained by bringing the media surface momentarily into a close proximity of a MO garnet material layer; (c) UV (365 nm) transmission-mode polarisation microscopy image of a 500 nm-thick MO garnet film with several imprints of credit card data stripes recorded magnetically inside the film layer, magnification X100. The stripes’ width is about 20 microns; (d) X1000 image of a small area of sample shown in (c), demonstrating the possibility of achieving sub-micron-scale imaging resolution.

After storing the digital media information within the film’s own domains magnetization distribution, high-contrast MO images can later be generated in either the transmission or reflection mode, without the necessity to keep the magnetized objects in contact with the imager films during inspection. Using UV polarization microscopy and MO films with very small domain size, ultra-high-resolution MO images can, in principle, be generated, which is expected to be useful for forensic data recovery from high-density magnetic recording media.

6.3 Magneto-Optic spatial light modulators for optical data processing

Recently magneto-optic (MO) light modulators or spatial light modulators (SLM) have become a prime research interest as they are very effective devices in optical
communication technology and information processing. They can be used to treat a large volume of data as a two-dimensional array for image recognition tasks, as well as in projector-assisted and holographic data representation. They can also be used as a component of future optical computing circuits. The basic principle of MO modulators is to modulate the light polarization using the Faraday effect. The polarization of a light beam passing through a MO material changes its direction if a magnetic field is applied to the materials as the off-diagonal dielectric permittivity tensor components change in response to the applied magnetic field. It is possible to modulate the amplitude of the transmitted optical field using a suitably oriented polarizer and analyzer pair placed on either side of the MO thin film material. Yttrium iron garnets are the most commonly used magneto-optic materials in spatial light modulators [139, 140].

Magneto-optic garnets and their nanocomposite garnet-type derivatives (synthesized by using RF sputtering or co-sputtering techniques followed by high temperature crystallization) can possess very high specific Faraday rotation in the visible spectral range and the attractive magnetic switching properties simultaneously, which opens the possibility of developing the current-driven pixellated MO devices for ultrafast image generation [141]. A 5x5 matrix of isolated MO pixels formed within a sputtered garnet layer using FIB milling and ion-beam-assisted conductor network deposition, and the polarisation microscopy images of a 3x3 and a 2x2 MO pixel arrays with magnetically-isolated pixels proposed for ultrafast image generation devices are shown in Fig. 6.8.
Fig. 6.8 (a) A 5x5 matrix of isolated MO pixels formed within a sputtered garnet layer using FIB milling; and (b, c) polarisation microscopy images of 3x3 and 2x2 MO pixel arrays with magnetically-isolated pixels for ultrafast image generation devices. All of these microdevice prototypes were designed and manufactured at ESRI, ECU during this research program.

These devices can be composed of magnetically-isolated pixel arrays in which the (remnant) magnetization states of each individual pixel need to be controlled individually. The pixel magnetization states can be controlled by a grid of conductors deposited, for example, by ion-assisted platinum (Pt) deposition within the focused ion beam (FIB) milled grooves formed in garnet films. The switching of individual magnetically-isolated pixels within the arrays has so far been demonstrated using external magnetic fields. Using the sputtered thin film garnet and garnet oxide composite materials having excellent MO properties therefore leads to the possible
building of large and arbitrarily-addressable pixel arrays which will find applications in ultrafast spatial light modulators and image recognition systems.

The development of these ultrafast spatial light modulators using fully-controlled arbitrarily-addressable magnetic pixel arrays (by applying external magnetic fields) has not been completed fully as yet. This project could be run for a couple of years to establish a set of technologies necessary to create these magnetically-controlled pixel arrays and also to achieve the capability to switch each of the pixels separately, which can represent an efficient and potentially revolutionary way of developing magneto-optic information displays and information processing systems.

6.4 Micro- and nano-structured magnetic field landscapes for cold atom manipulation

In the early 1960s, significant works were dedicated towards the cold/neutral atoms manipulation and confinement, and it was proposed for the first time that magnetic trapping of neutral atoms be used for various applications in the field of quantum information processing and quantum computing. A. L. Migdall et al made the first magnetic trap for neutral atoms in 1985 based on the development of modern laser techniques for atom cooling. The basic concept for the realization of tight magnetic traps was miniaturising the magnetic field producing elements and bringing the atoms close to the field source, which led to the development of atom chips and a hybrid atom chip has been constructed by using a perpendicularly magnetised GdTbFeCo thin film. This rare-earth transition material is also used by the Swinburne centre for creating the atom chips [142-144]. It is also possible to use permanently magnetised materials in the manufacture of atom chips. However, these atom chips can be engineered and created by manufacturing one-dimensional and two-dimensional periodic magnetic potentials (several micrometers-sized) on a device for trapping cold atoms, which is an alternative to using optical lattices for the same purpose.

Recently, the magnetic micro-traps have become very attractive and interesting in the area of condensed matter studies to manipulate cold atoms in quantum degenerate gases, such as Bose-Einstein condensate and ultra-cold fermions as magnetically-trapped ultra-cold atoms represent stable harmonic quantum systems. One of my research colleagues
(Dr Ahmed Abdelrahman, who has recently completed his PhD at ECU), used highly Bi-substituted gallium-doped dysprosium iron garnet which is defined by the chemical formula $\text{Bi}_2\text{Dy}_1\text{Fe}_4\text{Ga}_1\text{O}_{12}$ in his PhD research project and found the significance of this garnet material system for use as a permanent-magnet material which can be used to make new-generation two-dimensional magnetic lattices to trap and manipulate ultra-cold atoms. In his research work he explored a new method to realize and create a two-dimensional magnetic lattice having two different asymmetric configurations, which exhibited magnetic band-gap structure, and also a symmetric magnetic lattice. Fig. 6.9 shows a scanning electron microscope image of two-dimensional magnetic lattice containing 10x10 holes with dimensions $\alpha_h = \alpha_s = 10\ \mu\text{m}$ fabricated on a sputtered Bi-substituted iron garnet film of 1 $\mu\text{m}$ thickness deposited onto a 5 $\mu\text{m}$ thick silicon substrate. Also he described the tunneling mechanisms of magnetically-trapped ultra-cold atoms, prepared in a degenerate quantum gas state such as Bose-Einstein Condensate (BEC) in his publications [144-146].

![Fig. 6.9 Scanning electron microscope image of a fabricated two-dimensional magnetic lattice using a 1µm garnet thin film layer on a silicon substrate, this two-dimensional microstructure has been made by cutting 10 X 10 µm square holes on the garnet layer using the dual-beam Focussed Ion Beam (FIB/SEM) available at ESRI, Edith Cowan University [144].](image)

Bi-substituted gallium-doped dysprosium iron garnet ($\text{Bi}_2\text{Dy}_1\text{Fe}_4\text{Ga}_1\text{O}_{12}$) thin films are highly attractive not only because of having the flexibility of deposition process onto
various substrate types such as glass, GGG and silicon (Si) with the precise control over the film composition and thickness (one of the important parameters for designing an atom chip) but also for its important properties especially the magnetic and magneto-optic properties. Our record high-performance garnets possess high uniaxial anisotropy, nearly 100% remanent magnetisation, high coercivity (controllable by means of stoichiometry, film thickness and also the sputtering process parameters) as well as high MO quality in terms of figure of merit [23]. Layers of this novel material can be fabricated up to several microns in thickness with smooth and uniform surfaces of high quality, good thermal and environmental stability with high Curie temperature. In addition, these materials enable the observations of enhanced transversal magneto-optical Kerr effect (TMOKE) which was recently found in magneto-plasmonic structures and a report on this finding will soon be published elsewhere. All of the above features of this garnet type are the basic requirements for a material to be used as a permanent magnetic material. The combination of these excellent properties makes this garnet type very attractive for the development of atop chips besides all other emerging applications in integrated optics and photonics.

6.5 Potential application of garnets in biomedical sciences

Garnet thin films have a wide range of applications in biomedical and biological sciences including human implants and surgical tools such as imaging modalities, for example, the clinical tools MRI, CT, PET, ultrasound, etc. J. M. Talmadge *et al.* has described a technique for magneto-optical detection of weak magnetic fields by using bismuth-doped yttrium iron garnet (Bi:YIG) thin films based on the Faraday effect which proposed to overcome the limitations existing in currently available imaging modalities for the imaging of bio-magnetic fields. It has also been reported in literature that a Bi-substituted iron garnet layer of composition $Y_{2.5}Bi_{0.5}Fe_{5-d}Ga_dO_{12}$ ($d = 0.5–1$) prepared by liquid phase epitaxy has been used as a biocompatible magnetic thin layer onto which the biocompatible functionalised magnetic nanobeads have been deposited to study the cells-surface interactions which is currently considered as a promising biotechnological route in tissue engineering [147, 148].

Based on the domain structure of garnet films of easy-in-plane anisotropy, a device has been made for the transportation of magnetic microparticles which is very useful for microbiology, medicine and genetic engineering studies. Bismuth-substituted ferrite
garnet films of thickness 4 µm prepared by liquid phase epitaxy have been used to generate domain-wall tips to manipulate the magnetic particles, which can either drag or push the magnetic particles by the influence of applied external magnetic fields. These kinds of domain wall tips have potential applications in probing and manipulating colloidal systems [149, 150]. The control over the magnetic domains of garnet thin films by means of application of an external magnetic field helps modulate the generated magnetic field gradients existing on the film surface near domain walls, and also induces the controlled motion of colloidal particles placed above the film. The controlled transport of paramagnetic colloidal particles above magnetic garnet films can contribute significantly in several fields from targeted drug delivery to the realization of precise fluid-based micro-scale devices [151].

Highly bismuth-substituted iron garnet thin films (especially our newly-synthesised garnet nanocomposites) possess very high Faraday rotation as well as excellent optical and MO behaviour such as strong uniaxial anisotropy with excellent remnant magnetization property, variable magnetic domain configurations in changing external magnetic fields and the controllable coercive force values, as well as almost in-plane magnetization behaviour in some compounds. These classes of high-performance MO garnets are nontoxic, which indicates that it is possible to use this garnet for several emerging and promising applications in biomedicine. They are stable non-toxic thin film materials and will not have any effects on the cells or tissues to be examined by the strong magnetic field applied to magnetize the garnet thin films. High transparency across the visible spectral region of this class of MO garnet thin films (depending on the film thicknesses) is also an important parameter for the use of garnet thin films in biological investigations as most of the experimental works need the transmission-mode light microscopy. Under the influence of external magnetic field, light (passing through a MO material) undergoes a change in its polarization plane direction known as Faraday effect which can be employed for high-resolution MO imaging and sensing essential for applications such as digital forensics, security analysis, as well as biomedical engineering.

6.6 Summary

The emerging applications of different garnet materials are mentioned and the methodologies for future investigations towards improving their fabrication
technologies are described briefly. These classes of MO materials (in which the world-record performance characteristics were achieved in some single-layer thin film material types) can be the most important and essential parts for the future development of MO devices in integrated optics and photonics for a large range of applications. These MO garnets either having almost in-plane magnetization behavior, or the out-of-plane (perpendicular) magnetization direction can play vital roles for integrated optic device development if they can be prepared carefully according to the strict requirements imposed by these devices and also if the films’ quality is controlled (since high-quality thin films can only be achieved if they are prepared following the optimized deposition and annealing processes).
CHAPTER 7

CONCLUSION

This chapter presents the summary of findings, completes this thesis and also refers to some possible future initiatives suitable for consideration in optics & photonics research.

This thesis has presented a comprehensive investigation of the synthesis and characterization of highly bismuth-substituted iron garnet thin film materials and their application potential for various existing, emerging, and principally new applications in integrated optics and photonics. A comprehensive literature review has been conducted providing an overview of the theories and prior work related to the study of rare-earth iron garnets. Various fabrication processes and characterization technologies have also been discussed in the literature review sections.

A range of bismuth-substituted iron garnet thin-film materials having different bismuth substitution levels and metal dopants have been synthesized. The characterisation results of these newly-synthesized materials presented demonstrate the obtained low optical absorption losses, relatively high specific Faraday rotation, and also some control over the magnetic switching behaviour. These newly-synthesized MO garnet materials of two different composition types possess record-high MO figures of merit in conjunction with other excellent physical properties which make them very attractive for use in various integrated-optics and photonics applications.

7.1 Summary of the results achieved

The objectives of this research work which have been fulfilled and the obtained material development results presented in this thesis are as follows:

- Highly bismuth-substituted iron garnets of composition types (BiDy)₃(FeGa)₅O₁₂ and (BiLu)₃(FeAl)₅O₁₂ having out-of-plane magnetization and nearly in-plane magnetization behaviours have been synthesized.
• Bi-substituted iron garnet nano-composite garnet-oxide derivatives of these garnet material classes have been prepared by RF magnetron co-sputtering technique using two separate sputtering targets.

• The sputtering process parameters and the annealing regimes (both the temperature profiles and annealing durations) have been optimized to provide the repeatability of producing various high-quality garnet layers on various optically-transparent and also opaque substrates (dielectric, paramagnetic, amorphous and monocrystalline).

• Significantly lower optical absorption has been achieved in both classes of garnet thin film materials across the visible spectral range when compared to previously-reported materials of similar composition types. The obtained absorption coefficients in garnet materials of composition type (BiDy)$_3$(FeGa)$_5$O$_{12}$ were in the range of 1100-1300 cm$^{-1}$ at 635 nm, while the garnet materials of composition type (BiLu)$_3$(FeAl)$_5$O$_{12}$ exhibited around 2000 cm$^{-1}$ in the same spectral range.

• Substantially high specific Faraday rotations have been achieved across the visible spectral region, with more than 10 deg/µm demonstrated at 532 nm in films of (BiDy)$_3$(FeGa)$_5$O$_{12}$ composition type at remnant magnetization.

• Record-high magneto-optic (MO) quality factors in terms of the MO figure of merit have been achieved in both garnet subclasses, and the value of more than 50 degrees at 635 nm was obtained in composition type (BiLu)$_3$(FeAl)$_5$O$_{12}$.

• Strong uniaxial magnetic anisotropy (high magnetic memory) has been observed in the garnet material of the type (BiDy)$_3$(FeGa)$_5$O$_{12}$. MO images can be permanently recorded by making a brief contact with the objects under study using demagnetised garnet films.

• Controllable and moderately-high coercive force values (coercive force varied with the material composition and layer thickness) have been obtained in (BiDy)$_3$(FeGa)$_5$O$_{12}$ garnet layers.

• Comparatively much lower coercive force values have been obtained in (BiLu)$_3$(FeAl)$_5$O$_{12}$ garnet layers (coercivities of below 20 Oe achieved), also high Faraday rotations have been obtained in garnet of this composition type.

• High Faraday-effect magnetic field sensitivity defined by the ratio of increments of Faraday rotation to magnetic field obtained - up to 42.8°/(cm·Oe) at 635 nm wavelength in (BiLu)$_3$(FeAl)$_5$O$_{12}$ garnet layers.
7.2 Recommendations and future endeavours

There is the possibility of future work for further research exploration in the area of functional materials development, as well as in practical implementation of these garnet materials in optics and integrated photonics applications.

7.2.1 Design and development of all-garnet multilayer structures

Multilayer garnet thin film structures and nano-structured magnetic photonic crystals (MPCs) are very attractive due to their application potential in information technology and all-optical reconfigurable signal processing devices. It is always challenging to fabricate high-quality thin film nano-structures (of either single- or multi-layer type) with a good degree of control over their magnetic behaviour, especially if the magnetic switching behaviour and magnetic anisotropy properties need to be adjustable. RF magnetron sputtering allows precise controlling over the thin films deposition process parameters, thus reducing the problem of synthesizing high-quality thin films and multilayer structures wherein each layer's chemical composition (stoichiometry) must be controlled accurately [19, 56]. RF sputtered all-garnet multilayer structures (prepared using our two record-performance highly-Bi-substituted iron garnet material classes) can help realise the special magnetic behaviours which are not attainable using any single-layer thin films of a chosen garnet material type. The aim of this proposed work is to prepare garnet multilayer structures by sandwiching a magneto-soft garnet material in between two magneto-hard garnet materials with high bismuth substitution levels as well as optimized layer thicknesses and vice-versa. It is also proposed to engineer the magnetic properties in multilayers, especially the ways of adjusting the coercive force and magnetic anisotropy properties having different combinations of magnetization vectors within the material layers. These types of nano-engineered garnet multilayer structures are very important, and these are recently getting technological interest in multiple applications in nano-photonics and integrated optics, especially for the design of optical sensors and integrated optical isolators.
7.2.2 Design and development of optimized MPC structures by cutting air gaps inside MO garnet layers

Significant amount of research works (theory and practice-related) have been performed to investigate the properties of MPCs and their potential suitability for a range of applications in integrated-optics and photonics for communication and information technologies. The most commonly used MPCs are designed as symmetric cavity-type MPC and MPCs with multidefect having symmetric or non-symmetric sequence of thick magnetic and nonmagnetic layers (thickness of each layer is typically quarter-wavelength of optical thickness). However, these MPC structures are not frequently used in practice due to some limitations in MPC fabrication such as interlayer compatibility issues, thicknesses control requirements, and optimization of the overall fabrication process parameters including the deposition of multilayers and crystallization of entire structures. To overcome all of these barriers to the fabrication of MPC structures, next step would be to design and develop an optimized MPC structure (shown schematically in Fig 7.1) by cutting sequentially multiple air gaps inside a MO garnet layer sputtered onto the substrate (glass, GGG or silicon). A magneto-optic garnet layer (few microns in thickness) possessing excellent optical and MO properties in the visible and near-IR spectral regions will be sputtered and crystallized using an optimized annealing regime in a high-temperature oven annealing system. A focused ion beam (FIB) milling process will then be used to cut the air gaps within the garnet layer according to the pre-designed MPC structure, which can also be optimized using MPC optimization software packages.

![Fig. 7.1 Schematic diagram of an MPC structure incorporating the etched or milled “cut-outs” (air gaps) inside a sputtered MO garnet layer deposited onto a generic substrate.](image)
7.2.3 Amplification of MO behavior in MPC structures by introducing the rare-earth oxides into the MO photonic structures

High-performance MPC structures are always attractive for various applications in magneto-photonics and sometimes require the modification and improvements of either the MPC structures or the properties of MO garnet layers used within these structures. Amplification of MO properties of either the garnets or the MPC structures can be made possible by designing new photonic materials combining some photoluminescent rare earth oxides with MO garnet materials, or by designing MPC structures considering rare-earth oxides as an element of these structures.

Bi-substituted iron garnet thin-film materials themselves exhibit a strong potential for applications in various fields of science and frontier optical technologies. Rare-earth oxides are also very promising materials and exhibit photoluminescent (nanophosphors-type) properties. The next goal is to introduce the rare-earth oxides into the photonic systems which will help amplify the MO behaviour of the magnetic photonic structures by removing part of their absorption or scattering propagation losses [153]. These rare-earth oxide layers can be inserted into photonic systems either by co-sputtering with the garnet materials or by depositing the oxide layers (single or multiple) in-between the garnet multilayer structures.

7.2.4 Integration of MO functional materials within fibre optics and waveguides

Magneto-optic garnets are also very attractive for use in the integrated devices of interest for optical communication systems operating in the near-infrared region due to their strong Faraday rotation and simultaneously high MO figure of merit with low optical losses [83, 106, 154]. The next motivation is to deposit the MO functional garnets inside the optical fibre components and design novel MPC structures to make advanced nano-patterned functionalised waveguides or in-fibre polarisation rotators, as shown in Fig. 7.2. This concept of waveguide-integrated planar magnetic photonic crystals can be made possible by using focussed ion beam (FIB)-patterning of in-plane-magnetized garnet layers with good MO quality, which will allow the possibility of making new types of integrated light modulators and light controllers for different
applications. The optical fibre can be cut up to the fibre core using FIB milling process, and by using a collimated sputtering technique (which needs to be established in our labs), it is possible to fabricate a thick intra-fibre garnet layer, especially using the garnet having an almost in-plane magnetization behaviour and high MO performance. Later, an optimized planar MPC structure can be made within that in-fibre MO layer by using FIB-milling process. It is also possible to crystallize either the garnet layer or the MPC structure patterned within the garnet layer, using the conventional oven annealing processes.

![Fig. 7.2 The concept of waveguide-integrated planar magnetic photonic crystals; a small fibre cut-out made by using focussed ion beam (FIB) milling and a schematic diagram of an optimized MPC structure which can be designed and made within this sputtered MO garnet layer placed inside a fibre cut-out.](image)

7.3 Summary

The summary of the achievements made during this research work and some brief observations regarding the nature of the possible future efforts that can be considered as extensions of this work, as well as the practical applications of the findings obtained have been described.
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